Table of Contents

DEDICATION

This thesis is dedicated to my Mother (Late), who was my source of inspiration and I miss you so much

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Firstly, I am thankful to Almighty ALLAH for giving me strength and ability to complete this research work. I am also thankful to the administration of Faculty of Textile Engineering, Technical University of Liberec, Czech republic, for giving me this unique opportunity to weave my ideas to reality under the guidance of learned faculty. Upon completing this dissertation, I owe my deepest gratitude to so many people for their immense assistance. I would like to begin by expressing my deepest gratitude to my supervisor, Ing. Jana Saskova PhD and specialist Professors, Prof. Ing. Jiri Militky CSc Euring and Prof. Ing. Jakub Wiener PhD, for their encouragement, mentoring, support, cooperation and focused discussions throughout this work. They have helped me to realize the importance of distilling and presenting my ideas in a coherent and accessible fashion. They have also extended their support me at every step throughout my stay at Technical University of Liberec.

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Lastly, but not the least I can never forget my parents and family especially my father, wife and son Aarib who really suffered the effects of isolation during my stay away from home.

ABSTRACT

Polyester is the most widely used material for both textile and non-fibrous applications. The major potential applications are high mechanical strength, good stretchability, heat stability, rapid drying, wrinkle resistance and resistance to usual organic solvents. The inherent hydrophobic nature of the polyester products are lacking water and moisture wicking, poor adhesion properties and ability to develop static charge. The modification of surface of the polyester by low concentration alkaline hydrolysis with NaOH in aqueous finishing bath under hot drying conditions is explored in this study. Moreover the surface of polyester film is modified by synergistic effect of sulphuric acid and sodium hydroxide in order to achieve hydrophilic surface with improved adhesion. The use of chemicals allows the surface hydrophilization of polyester at conventional pad-dry stenters without use of any sophisticated equipment that is required by most of the physical modifications (like plasma, corona, ozone etc).

The surface hydrophilization of polyester fabric is done by low concentration of sodium hydroxide. The time of treatment, curing temperature and concentration of sodium hydroxide played very important role in getting better wicking rate and stability of the treatment. The weight loss of the fabric is minimized through the low liquor ratio pad-dry method of application. The use of hygroscopic agents like glycerin and urea at elevated temperatures has contributed to retain humidity during hot dry reaction conditions. The weight loss is far less than the high liquor ratio alkali treatment of polyester fabric. In this work optimization of parameters for getting higher vertical wicking rate and less surface scission through weight loss has been achieved by varying concentration of sodium hydroxide (20, 35 and 50 g/l), time of treatment (2,4, and 6 minutes) and drying temperature (130, 150 and 170 ˚C). Later the stability of the surface hydrophilization is evaluated at different temperatures by placing for longer times. The hydrophilized polyester fabric surface shows good stability at different temperatures and in comparison with plasma and ozone surface hydrophilic treatment. The activated polyester fabric shows good fastness against number of washing cycles. The surface morphology and chemical characterization of the hydrophilized polyester fabric is measured by Scanning Electron Microscope (SEM), X-ray Photoelectron spectroscopy (XPS) and Brunauer Emmett Teller (BET).

The polyester film is hydrophilized with strong sulphuric acid solution and followed by low concentration alkali solution to evaluate the surface wettability and adhesion properties. The super

hydrophilic surface is obtained at 80 % sulphuric acid and 50 g/l sodium hydroxide aqueous solution treatment. These treatment conditions give the polyester film surface with lowest water contact angle and high SFE values with good adhesion properties. The presence of hydroxyl groups on the surface with significant decrease in the surface energy has been confirmed through contact angle measurements. The SEM, BET analysis and T-peel data obtained by the polyurethane resin has indicated the increase in adhesion strength after chemical treatment and improvement of adhesion by thermoset resin can be attributed to the increase in surface wettability and roughness due to the surface modification.

Key words: Polyester, hydrophilized surface, optimization, stability, vertical wicking, wettability, roughness

ABSTRAKT

Polyester je nejrozšířenějším materiálem jak pro textilní, tak pro nevlákenné aplikace. Hlavní potenciální aplikace předurčuje vysoká mechanická pevnost, dobrá tažnost, tepelná stabilita, rychlé sušení, nemačkavost a odolnost vůči obvyklým organickým rozpouštědlům. Vlastní hydrofobní povaha polyesterových výrobků bez přítomnosti vody a vlhkosti zapříčiňuje špatné adhezní vlastnosti a schopnost vytvářet statický náboj. Modifikace povrchu polyesteru alkalickou hydrolýzou s nízkou koncentrací NaOH ve vodné dokončovací lázni za podmínek sušení za tepla se zkoumá v této studii. Navíc je povrch polyesterové fólie modifikován synergickým účinkem kyseliny sírové a hydroxidu sodného, aby se dosáhlo hydrofilního povrchu se zlepšenou přilnavostí. Použití chemikálií umožňuje povrchovou hydrofilizaci polyesteru na konvenčních zařízeních bez použití sofistikovaného vybavení, které vyžaduje většina fyzikálních modifikací (jako je např. plazma, korona, ozón apod.)

Povrchová hydrofilizace polyesterové tkaniny se provádí nízkou koncentrací hydroxidu sodného. Doba úpravy, teplota sušení a koncentrace hydroxidu sodného hrály velmi důležitou roli při získávání vyšší vzlínací rychlosti a stability úpravy. Úbytek hmotnosti tkaniny je minimalizován aplikací suchého způsobu nanášení na suchý podklad. Použití hygroskopických činidel, jako je glycerin a močovina, při zvýšených teplotách přispělo k udržení vlhkosti při reakčních podmínkách sušení za zvýšených teplot. Ztráta hmotnosti je mnohem nižší, než je poměr vysokého obsahu alkoholu při alkalickém zpracování polyesterové tkaniny. V této práci byly optimalizovány procesní parametry pro dosažení vyšší vertikální rychlosti nasákavosti a nižšího narušení povrchu sledovaného prostřednictvím úbytku hmotnosti, a to pomocí změny koncentrace hydroxidu sodného (20, 35 a 50 g/l), doby zpracování (2, 4 a 6 minut) a teploty sušení (130, 150 a 170 °C). Stabilita povrchové hydrofilizace se sleduje po delší dobu, při různých teplotách. Hydrofilizovaný povrch polyesterové tkaniny vykazuje dobrou stabilitu při různých teplotách a ve srovnání s hydrofilním zpracováním povrchu plazmy a ozonu. Aktivovaná polyesterová tkanina vykazuje dobrou stálost vůči počtu pracích cyklů. Morfologie povrchu a chemická charakterizace hydrofilizované polyesterové tkaniny se měří pomocí skenovacího elektronového mikroskopu (SEM), rentgenové fotoelektronové spektroskopie (XPS) a Brunauer Emmett Teller (BET).

Polyesterová fólie se hydrofilizuje silným roztokem kyseliny sírové a následně působením alkalického roztoku o nízké koncentraci za účelem průzkumu povrchové smáčivosti a adhezních

vlastností. Superhydrofilní povrch se získá při použití 80% roztoku kyseliny sírové a 50 g/l vodného roztoku hydroxidu sodného. Tyto podmínky zpracování poskytují polyesterovému povrchu fólie nejnižší kontaktní úhel smáčení vodou a vysoké hodnoty SFE s dobrými adhezními vlastnostmi. Přítomnost hydroxylových skupin na povrchu s výrazným poklesem povrchové energie byla potvrzena měřením kontaktního úhlu. SEM, BET analýza a T-Peel data získaná s využitím polyuretanové pryskyřice naznačila zvýšení adhezní síly po chemickém zpracování a zlepšení adheze termosetovou pryskyřicí lze přičítat nárůstu smáčivosti povrchu a zvýšení drsnosti díky povrchové modifikaci.

Klíčová slova: polyester, hydrofilizovaný povrch, optimalizace, stabilita, vertikální vznícení, smáčivost, drsnost

خلاصہ

پولیسٹر ایک ایسا پولیمر ہے جو روزمرّہ زندگی میں ٹیکسٹائل اور بے شمار اشیأ میں استعمال ہوتا ہے۔ اس کا کثرت سے استعمال کیا جانا اس میں پائی جانے والی خصوصیات کی وجہ سے ہےجیسا کہ مضبوطی، بہتر لچک، جلد خُشک ہونا، کم سلوٹیں پڑنا اور بہت سارے کیمیائی محلول میں غیرحل پذیر ہوسکنا۔ پانی کو اپنے اندر جزب نہ کرنے کی صلاحیت کی وجہ سے پولیئسٹر سے بننے والے کپڑے میں پسینہ جزب نہیں ہوتا جو کہ انسان کے لیے غیر اطمنان بخش صورت حال پیدا کرتا ہے۔ اگر کسی الکلی کے محلول کو پولیئسٹر پر لگایا جائے تو اس کی سطح پر پانی جزب کرنے کی اور چپکنے کی صلاحیت بڑھ جاتی ہے۔ اس تجرباتی کام میں پولیئسٹر کپڑے پر سٹنٹر کی مدّد سے سوڈیم ہائیڈرو آکسائیڈ لگایا گیا ہے۔ پولیئسٹر کے ورق پر تیزاب اور سوڈیم ہائیڈرو آکسائیڈ کی مدّد سے بہتر جزب کرنے والی سطح حاصل کی گئی ہے۔

سوڈیم ہائیڈرو آکسائیڈ کی مدّد سے پولیئسٹر کو ہائیڈرو فیلائیزڈ سطح میں تبدیل کیا گیا ہے۔ الکلی کا ارتکاز،تعمل کا وقت اور درجّہ حرارت کی تبدیلی سے کپڑے میں پانی کی عمودی رطوبیت، وزّن کا کم ہونا اور استحکام حاصل کرنے میں اہم کردار ادا کیا۔ پیڈ ڈرائی اصلاحی طریقہ کار سے کپڑے کے وزّن میں کم شرح تناسب سے کمی ہوئی ہے۔ پانی کو ہوّا سے جزب کرنے والے مادے گلییسرین اور یوریا نے بھی کپڑے کی سطح کو بہتر کرنے میں اہم کردار ادا کیا۔بعد میں سطح کے ہائیڈرو فلائزیشن کے استحکام کو طویل درجہ تک رکھنے کیلیے مختلف درجّہ حرارت پر اس کا جائزہ لیا گیا ہے۔پولیئسٹر کپڑے نے پلازمہ اور اوزُون کے مقابلہ میں ہائیڈرو فلائزڈ استحکام کو مختلف درجّہ حرارت پر بہتر طور پر برداشت کیا ہے۔ فعال شدہ سطح کی مارفولوجی اور کیمیائی خصوصیات کی جانچ XPS, BET اور SEM سے کی گئی ہے۔

پولیئسٹر ورق کو قلمی شورہ کے تزاب اور سوڈیم ہائیڈرو آکسائیڈکے محلول سے افزدہ کیا گیا ہے۔ اس تجربہ میں ۸۰فیصد قلمی شورہ کا تزاب اور ۵ فیصد سوڈیم ہائیڈرو آکسائیڈ محلول سے پانی جزب کرنے والی سطح حاصل کی گئی ہے۔اس لگانے کے طریقہ سےپانی کا تماسی زاویہ اور سطح کی توانائی میں کمی آئی ہے۔ ورق کے چپکنے کی صلاحیت بہتر ہوئی ہے۔ SEM, BETاور T-PEEL ٹیسٹ سے بھی اس بات کو تقویت ملی ہے کہ پولیئسٹر ورق کی چپکنے کی صلاحیت اور سطح کی نرمی میں واضح طور پر بہتری آئی ہے۔

کلیدی الفاظ:۔ پولیئسٹر، عمودی رطوبیت، ہائیڈرو فلائزڈ سطح، اصلاحی طریقہ کار، سطح کی نرمی، استحکام

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS / SYMBOLS

PET	Polyethylene Terephthalate (polyester)
CA	Contact Angle
SFE	Surface Free Energy
BET	Brunner Emmett Teller
SEM	Scanning Electron Microscopy
XPS	X-Ray Photoelectron Spectroscopy
SHC	Sodium Hydroxide Concentration
WL	Weight Loss
APP	Atmospheric Pressure Plasma
SHC	Sodium Hydroxide Concentration
TEMP	Temperature
DF	Degree of Freedom
SS	Sum of Squares
MS	Sum of Mean Squares
SH	Suction Height
γ	Surface Tension
∇	Del, Gradient Operator
ρ	Density

CHAPTER 1
INTRODUCTION

Polyethylene terephthalate (PET) is one of the most important and widely used material in both textile industry for its apparel applications and in nonfibrous applications. They have properties like easy care, high strength, suitability for blending with other hydrophilic fibers, dimensional stability, thermal and chemical resistance, these properties make polyester fibers useful for versatile applications in the textile industry. Polyester fibers have taken the major position in textiles all over the world but they have some drawbacks like low moisture regain, static electricity accumulation, poor soil release properties, formation of pills on the garment. Research work is done in order to minimize the abovementioned deficiencies in the polyester by the controlled alkali treatment of the polyester fibers and fabrics through exhaust method [1-3] and hydrolysis of PET by strong acid or alkali [4], amine treatment [5], alcholysis [6] and treatment by various radiations including plasma [7, 8].

The modification of polyester surface is field to achieve hydrophilicity and surface that has specific characteristics to be used to provide better suitability for the use of adhesives [9], biomaterials [10] and protective coatings [11]. Polyester fabrics have attained highest popularity among different blends because of good all-round performance and attractive price. Addition of polyester in the blend improves the fabric performance, wrinkle recovery and durability but with a sacrifice of comfort properties of the fabric. Several attempts have been made to enhance the comfort properties of pure polyester fabrics including the caustic treatment with sodium hydroxide. Polyester is hydrolyzed by aqueous sodium hydroxide and undergoes nucleophilic substitution reaction as hydroxyl ion attacks carboxyl carbon of polyester following the chain scission results in production of hydroxyl and carboxylate end groups. This attack occurs at surface of fiber and loss in weight of fiber occurs [12] The strong acid causes micro scale roughness on the surface of PET that can then be used for further treatment of the polyester. In this study the acid treatment of polyester is done and then followed by alkaline hydrolysis and its effect on contact angle and surface energy is studied.

Desirable performance at the workplace, durability and long service life are some of the key characteristics required from the workwear fabrics. In comparison to formal dress shirts, workwear

apparels have to bear more taxing conditions not only in wearing but also during laundering. In order to meet these stringent requirements, workwear apparels are often made from a bit heavier fabrics having higher yarn linear densities as well as fabric densities, compared to formal dress shirts. Heavier fabric construction gives better performance properties to workwear but usually at the cost of comfort properties. The property of absorbing moisture is a valuable feature of clothing materials. Apart from its direct utility in keeping the skin dry, the absorption of water causes the fabric to act as a heat reservoir, protecting the body from sudden changes of external conditions. However, it may be a disadvantage in drying the hygroscopic fibers that it is necessary to remove the absorbed moisture that is not present in the non-hygroscopic synthetic fibers [13].

Wetting and wicking are important phenomena in the processing and applications of fibrous materials. Various aspects of liquid–fiber interactions such as wetting, transport, and retention have received much attention both in terms of fundamental research and for product and process development. A spontaneous transport of a liquid driven into a porous system by capillary forces is termed wicking because capillary forces are caused by wetting; wicking is a result of spontaneous wetting in a capillary system. Wetting is a prerequisite for wicking. A liquid that does not wet fibers cannot wick into a fabric. The wetting and wicking behavior of the fibrous structure is a critical aspect of performance of products such as sports clothes, hygiene disposable materials, and medical products [14]. Wetting and wicking processes occurring during wearing of clothes have a practical significance in clothing comfort.

The interaction of liquids with textile have some fundamental physical phenomena: wetting of the fiber surface, transport of the liquid into assemblies of fibers, adsorption of the fiber surface, and diffusion of the liquid into the interior of the material. The water vapor that is to move in a fibrous medium, it must wet the fiber surfaces before being transported through the interfiber pores by means of capillary action. The molecules on the surface of a liquid experience an imbalance of forces. Hence, there is presence of free energy at the surface of the liquid. The excess energy is called ‘surface free energy’, for a liquid to wet a solid completely, or for the solid to be submerged in a liquid, the solid surfaces must have sufficient surface energy to overcome the free surface energy of the liquid. The surface free energy can be quantified as a measurement of energy per area. It is usually termed surface tension’ and is quantified as force per length, with units mN/m or dynes/cm [15].

Over the last few decades, many advances have been made in developing surface treatments by plasma, corona, flame, photons, electrons, ions, X-rays, gamma-rays, and ozone to alter the chemistry of polymer surfaces without affecting their bulk properties. Plasma treatment, in air or oxygen environment, corona and flame treatments are the most designated techniques in oxidation of surfaces of polymers. In both plasma and corona treatments, the accelerated electrons bombard the polymer with energies 2-3 times that necessary to break the molecular bonds, producing free radicals which generate cross-linking and react with surrounding oxygen to produce oxygen-based functionalities. Polar groups being typically created on the surface are hydroxyl, peroxy, carbonyl, carbonate, ether, ester, and carboxylic acid groups [16]. In flame treatment, surface combustion of polymer takes place with formation of hydro peroxide and hydroxyl radicals. Oxidation depth through flame treatment is around 510 nm, and over 10 nm for air plasma treatment. Plasma, corona and flame treatments end in extensive surface oxidation and results in highly wettable surfaces [17]. Polar groups produced during surface oxidation have tendency to be buried away in the bulk when in contact with air for extended period of time, but they remain on the surface when in contact with water or any other polar environment. Alkali treatment of polymers, especially at elevated temperature, can also enhance surface hydrophilicity of polymers. Hydroxyl and carboxyl groups are among the hydrophilic groups formed on the surface of polymers such as polyolefins and polyethylene terephthalate during their etching with concentrated bases [18].

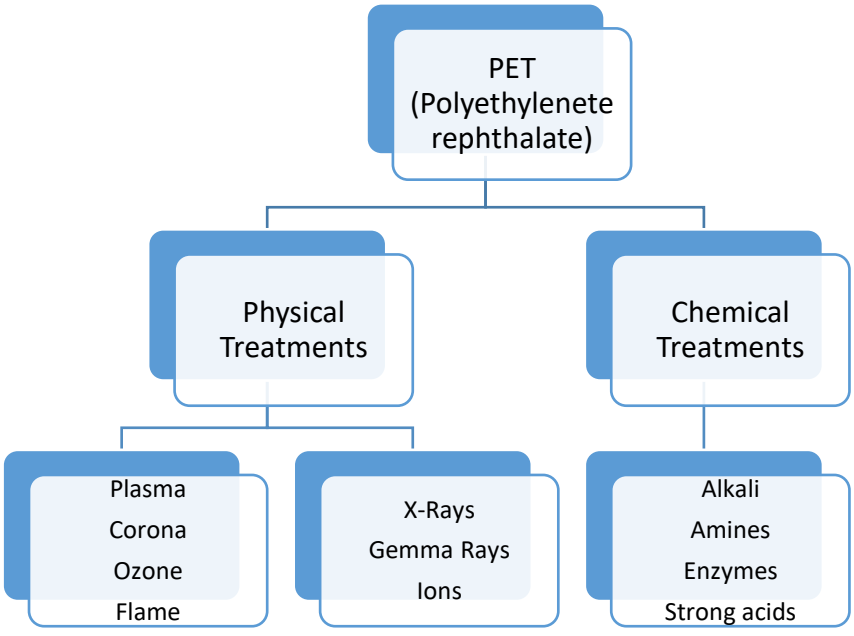


Figure 1. Summary of treatments carried out for polyester surface modification

The terms “hydrophilic surface” and “hydrophobic surface” appeared in the literature many decades ago and they are commonly used to describe opposite effects of the behavior of water on a solid surface. A hydrophilic surface has strong affinity to water whereas hydrophobic surface repel water. This simple definition however, is too general for the classification of a variety of different solids having different wetting characteristics, typically studied in three-phase systems with water and air or water and oil as fluids. Water (or other polar liquid) is preferred on hydrophilic surface over a nonpolar phase such as air or oil. It is established that 90 degrees of water contact angle measured in air environment is traditionally a popular cut between hydrophilic and hydrophobic surfaces; hydrophobic surface when water contact angles is larger than 90 degrees ($\theta>90^o$) and hydrophilic one with contact angles of $\theta<90^o$.

The weight reduction of polyester fabric is usually done by the exhaust method under high liquor ratio [19, 20]. This leads to the longer cycle time and more weight loss of the polyester fabric. The padding technology is a well-known process in the field of polyester and cotton fabric processing. The padding and drying technology involve the use of less liquor and higher production rate at high temperature. The padding technology in dyeing and finishing of polyester is widely used in order to save the liquor and achieving more smooth fabric properties with high reproducibility [21]. The alkaline treatment of polyester fabric is carried out by padding method at low concentration with the objective to study the effect of different treatment conditions on the surface hudrophilization and physical characteristics of polyester fabric and polyester film.

CHAPTER 2
RESEARCH OBJECTIVES

2.1 Research aims

The research aims of this study are

a) **To study the effect of different hygroscopic agents on alkali treatment of polyester fabric by Pad-dry method**

   The objective is to treat polyester fabric with sodium hydroxide and different hygroscopic agents, like glycerin and urea, by dry heat treatment method at low padding liquor ratio. The main focus is to evaluate the surface hydrophilization of polyester through wicking and effect of sodium hydroxide treatment on the weight loss of polyester fabric. The low concentration alkali treatment is carried out and effect of parameters, time and temperature, on alkali hydrolysis is studied.

b) **To optimize parameters for surface hydrophilization of polyester fabric by dry heat fixation method**

   The objective is to optimize the parameters for surface hydrophilization of polyester fabric for getting higher values of wicking and lower percentage weight loss at specified conditions. Different parameters like sodium hydroxide concentration (SHC), time of treatment (TIME) and temperature of hydrolysis (TEMP) significantly affect the functional characteristics like wetting of fabric, vertical wicking rate and percentage weight loss of hydrophilized polyester fabric. The purpose is to optimize the reaction conditions for better wettability of the polyester fabric.

c) **Performance and durability of optimized pad-dry heat sodium hydroxide treated polyester fabric at different temperature conditions**

   The vertical wicking of optimized sodium hydroxide treated polyester fabric is evaluated by placing at different temperature for longer periods of time and then compared with physical treatments like plasma and ozone. The high temperature stability of the chemical alkali treatment is generally high due to the generation of hydrophilic groups on the surface

of the polymeric substrate. The physical treatments generally activate the polymeric surface that is susceptible to reverse at elevated temperatures. The objective of this evaluation is to check the durability of the sodium hydroxide treatment by padding technology.

d) Development of super hydrophilic surface of polyester film by combined acid and alkali treatment

The objective is to prepare porous polyester film by synergistic effect of strong acid and sodium hydroxide treatment that can have a superhydrophillic surface for adhesion improvement. The acid treatment creates roughness on the surface of the polyester film that provides sodium hydroxide to penetrate easily and hydrophilized the surface of film in lesser time. The film surface is then evaluated for the contact angle, surface free energy, T-Peel test of adhesion and BET specific surface area analysis.

CHAPTER 3
LITERATURE REVIEW

Polyester fibers are Man-made fibers that are composed of long chain polymer containing at least 85% by weight of an ester of dihydric alcohol and terephthalic acid. Polyester fibers have applications in clothing sector like easy-care, wash-and-wear, and durable press garments. It had excellent wrinkle recovery both in wet and dry state.

Polyester fibers have taken the major position in textiles all over the world although they have many drawbacks e.g., (a) low moisture regain (0.4%), (b) the fibers has a tendency to accumulate static electricity, (c) the cloth made up of polyester fibers picks up more soil during wear and it also difficult to clean during washing, (d) the polyester garments from pills and thus, the appearance of a garment is spoiled, (e) the polyester fiber is flammable. Thus, it has been suggested that surface modifications can have an effect on hand, thermal properties, permeability, and hydrophilicity [22].

3.1 Alkali treatment

Polyester fabrics have been widely accepted by consumers for their easy care properties, versatility and long life. Inspite of such acceptance, complaints concerning their hand, thermal properties and moisture absorbency have been cited. Improved moisture absorbency of polyester fibers can be achieved by introducing hydrophilic block copolymers. However, this modification can lead to problems of longer drying time, excessive wrinkling and wet cling. In addition, penetration of water into the interior of the fibers has not been clearly shown to improve perceived comfort. It has been suggested that surface modifications can have an effect on hand, thermal properties, permeability, and hydrophilicity.

Polyester fibers are prone to the action of bases depending on their ionic character. Bases like caustic soda, caustic potash and lime water have tendency to effect the outer surface of polyester filaments. Primary and secondary bases and ammonia can diffuse into polyester fiber and attack in depth resulting in breaking of polyester chain molecules by amide formation. One of the surface modifications is the controlled hydrolysis of polyester. The action of strong base leads to cleavage of ester linkages on the fiber surfaces. The result is the formation of terminal hydroxyl and

carboxylase groups on the fiber surface. Hydrolysis is believed to increase the number of polar functional groups at the fiber surface.

The modification of polyester by caustic soda is a widely used technique to improve comfort properties of fabrics. This technique was patented soon after the invention of polyester [23]. Polyester is hydrolyzed by aqueous sodium hydroxide and undergoes neucleophilic substitution reaction as hydroxyl ion attacks carboxyl carbon of polyester following the chain scission results in production of hydroxyl and carboxylate end groups. This attack occurs at surface of fiber and loss in weight of fiber occurs. The reaction of alkaline hydrolysis is shown in figure 2 [24].

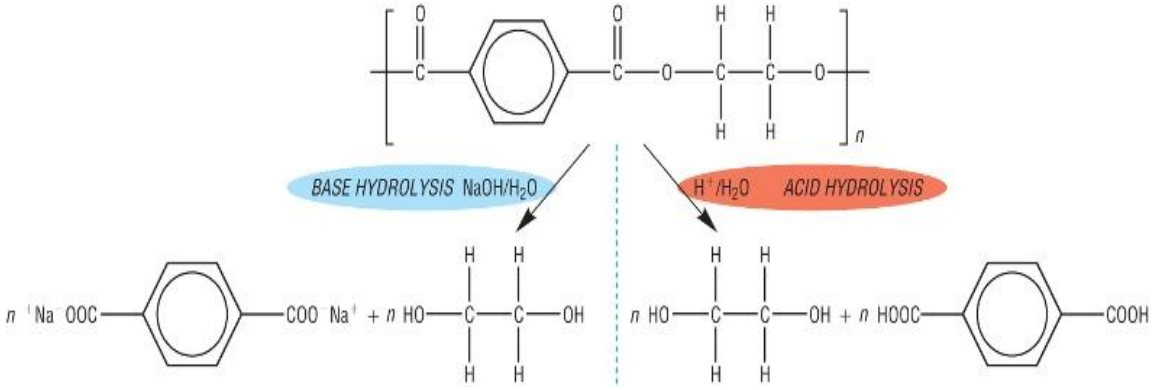


Figure 2. Mechanism of alkaline and acid hydrolysis of Polyethylene terephthalate (Polyester)

The major contribution in the research about alkali treatment of polyester is uncovered in review performed by Zeronian and his coworkers (1988, 1990). Walters (1950) was the first investigator to carry out work on the alkaline hydrolysis of polyester yarns. Zeronian and Collins (1988) demonstrated that weight loss of polyester fibers enables us to study the fine structure of polyester fibers.

The NaOH treatments significantly increased the ability of the PET fabric to transport water from the fabric surface into the interior of the fabric thus increasing the height of the water that is wicked through vertically held strips of the fabric. The water drop absorption time decreases sharply after weight reduction with NaOH thus increasing the wettability and soil release properties of polyester fabric. The wettability increase in polyester after weight reduction is due to the significantly decrease in the contact angle of water with the surface of polyester.

The alkaline hydrolysis of PET fibers is carried out with an aqueous alkaline solution, such as sodium hydroxide (NaOH). In the alkaline hydrolysis process, PET undergoes a nucleophilic

substitution as shown in figure 3 [25] and is hydrolyzed with NaOH. Chain scission of PET occurs, resulting in a considerable weight loss and the formation of hydroxyl and carboxylate end groups [26], which improves the handling of the fabric and its moisture retention, and allows the surface of fabric to generate hydrophilic groups.

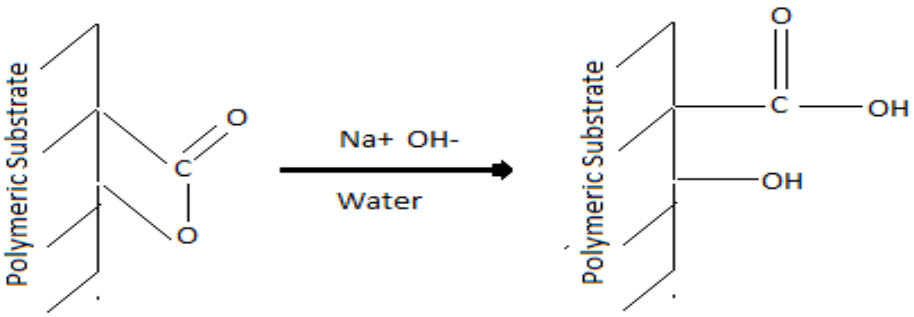


Figure 3. Scheme of nucleophilic substitution of the hydroxide ion to the carboxyl groups

3.2 Weight loss of polyester

During the hydrolysis of PET, the percentage loss in weight, linear density, tenacity and elongation at break maintains a lower linear profile when the reaction temperature remains below the glass transition [27] temperature (Tg) of PET. Above Tg, these parameters show a rapid increase with temperature. This is confirmed from the work carried out by Datye et al [28], who found that the transition temperature for weight loss upon hydrolysing PET yarn for 40 minutes in 1 N NaOH is 65 °C. It is believed that the steep rise in weight loss above the glass transition temperature is partly due to the increased sequential mobility of the PET polymer chains. When considering the process of alkaline hydrolysis of polyester, the relative importance of different reaction parameters appear to be in the following order:

Treatment time < Concentration of alkali < Treatment temperature

The studies carried out by Namboori [29] showed that at 60, 80 and 100 °C the percent weight loss of PET fiber depended on the initial concentration of alkali and showed a linear relation with respect to time of treatment. He recorded a 5% weight loss after treating PET fibers at 60 ˚C in NaOH for 60 minutes. The percent elongation at break decreased considerably, whereas the tenacity at break showed only a small change. The hydrolysis carried out in alkali (NaOH) medium on PET film showed an increase in density which was less than in the case of acid treatment. It also showed a higher increase in crystallinity than had been expected from density data. When the

concentration of NaOH was increased from 5 to 15% at a constant temperature of 60 ˚C after 3 hours of degradation time the crystallinity increased slightly. With a 5% (wt/vol) NaOH concentration, the samples were completely destroyed after 6 hours at 90 ˚C. End group analysis showed that the alkali did not cause random chain scission as in the case of acid hydrolysis found that as the density of bright PET yarns increased with heat setting, the rate of weight loss decreased [30]. For the given test parameters, no major changes in differential molecular weight distribution (DMWD) were recorded. For all samples, the density of the hydrolyzed fibers increased with longer times of hydrolysis. The semi dull fibers showed a significantly more rapid increase than the bright fibers.

The equation 1 represents the density of successive layers in the radii of the original and final (hydrolyzed) fibers. Again it is assumed that fibre length does not change during hydrolysis.

$$\rho_t = \rho_1 \left(1 - \frac{r_c^2}{r_t^2}\right)^n + \rho_1 \left(\frac{r_c^2}{r_t^2}\right)^n \quad (1)$$

Where $\rho_1$the density of is removed layer, ρ_t is the density of starting product, r_c and r_t are the radii of remaining core and starting fiber respectively.

The weight reduction of polyester fiber does not change the cross section of fiber as indicated by the electron microscopic analysis of the fibers after reduction in weight of polyester fibers by caustic treatment. A loss in weight and surface pitting of polyester occurs after the alkali treatment. As concentration of alkali and the time of treatment increase the weight loss of polyester increases. The study of 100% polyester rotor spun yarns with different TMs (3.0, 3.5, and 4.0) treated with 5%, 10%, and 15% NaOH concentrations at 60° C and 100°C for 30 min is carried out. The results of the study show that the weight losses registered an increasing trend as the concentration of NaOH increased and the rate of hydrolysis registered a decreasing trend as the yarn TM increased from 3.0 to 4.0 at 60° C and 100 ° C treatment conditions, respectively[31].

The effect of pretreatments on the hydrolysis and physical properties of polyester has been investigated [24] and it is found that the solvent treatment with pretreatment reagents (benzyl alcohol (PET-b) or 2-phenyl ethanol (PET-p) can modify the structure of the PET fabrics. Fabric weight loss has the linear positive relation with increasing hydrolysis time. The rate constant (K) increased markedly with increasing methyl groups in the pre-treatment reagents. The activation energy (Ea) of untreated fabrics was higher than that of the treated fabric. The crystallinity of the

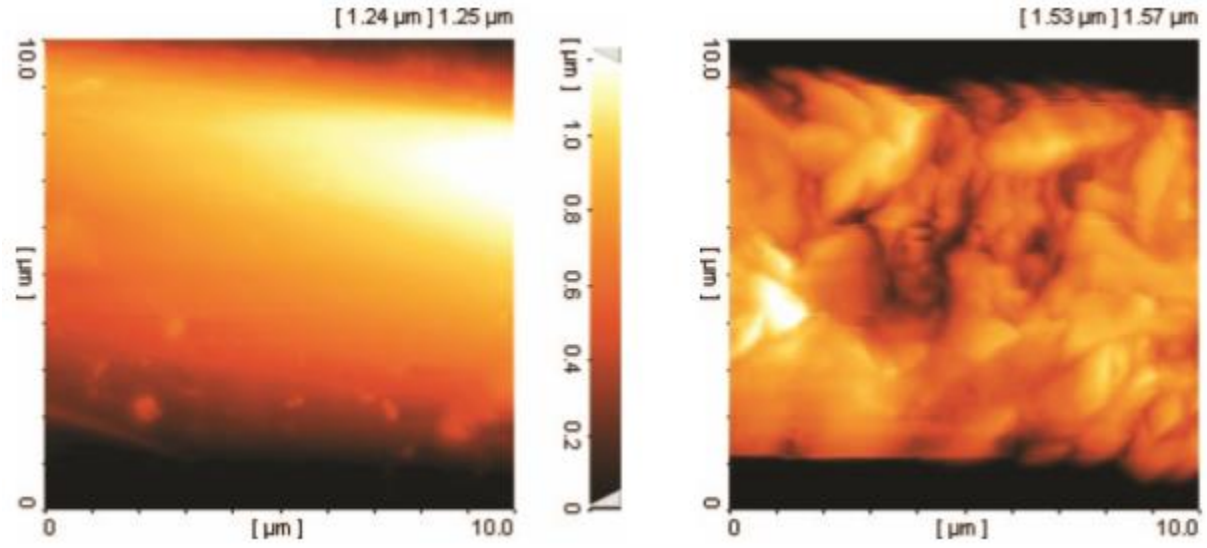
PET fabrics increased with increasing hydrolysis times (t) and methyl groups in the pretreatment agents. The weight loss of PET-b increased with increasing pretreatment temperature (T). However, the weight loss of PET-p increased upto 100°C but decreased above 120°C. The shrinkage value- of all samples increased with increasing hydrolysis times (t). Shrinkage values of PET-b and PET-p were greater than those of untreated fabrics. PET-b displayed greater shrinkage than PET-p because byproducts polluted the PET fibres. Both the initial and maximum water absorption of the fabrics increased with increasing hydrolysis times (t). Thus these two reagents, namely, benzyl alcohol and 2-phenyl ethanol have modified the structure of polyester fibres. 2-phenyl ethanol contributed more effectively to the weight loss and crystallisation of PET than did benzyl alcohol. It is pointed out by the authors that these effects on weight loss, crystallinity shrinkage and water absorption caused by 2phenyl ethanol can be attributed to pollution with byproducts at pretreatment temperatures above 120°C. The effect of pretreatments on weight-reduced fabrics and chain scissoning of PET that results in a considerable weight loss and formation of hydroxyl and carboxylate end groups has been the area of study to quantify the treatment [32].

3.3 Effect of alkali treatment on yarn and fabric properties

The investigation on hydrolytic degradation of PET (polyethylene terephthalate) has carried out. The importance of degradation in the drying of PET before processing and the loss of weight and mechanical properties has been discussed [33]. Several techniques were used to investigate the hydrolytic degradation of polyester and its effect on changes in molecular weight. Hydrolytic conditions were used to expose fiber-grade PET chips in water at 85 ºC for different periods of time. Solution viscometry and end-group analysis were used as the main methods of determining the extent of degradation. The experimental results have shown that polyester is susceptable to hydrolysis. Also, it was found that as the time of retention in hydrolytic condition increased, the molecular weight decreased, but the rate of chain cleavage decreased to some extent, at which point there was no more sensible degradation. The moisture content obtained confirmed the end group analysis and viscometry results. Predictive analytical relationships for the estimation of the extent of degradation based on solution viscosity and end-group analysis are presented.

The alkali treatment of polyester has effect on the weight of the fabric. A loss in weight and surface pitting of polyester occurs after the alkali treatment. The weight reduction of polyester fiber does

not change the cross section of fiber, slight loss in weight and decrease in mechanical properties is reported. Mousazadegan [34] have reported on the effect of alkaline hydrolysis treatment on the physical and mechanical properties of microfiber polyester fabric. A polyester fabric made from 150 d/144 textured filament was used in both warp and weft directions. The baths were prepared by using different concentration of laboratory grade of sodium hydroxide with 4, 6, 8, 10 and 12 g/l concentration Quaternary ammonium compound was used as an accelerator The fabrics were tested for weight reduction, bending length, crease recovery angle, air permeability, yarn strength, fabric strength, fabric thickness, tear strength, fabric drape, fabric abrasion, fiber diameter, yarn crimp, fabric areal density and fabric roughness. It was found that as the weight reduction is increased the fabric weight fell. Weight reduces with an increase in sodium hydroxide concentration. Drape is found to decrease with an increase in weight reduction of fabrics. All the mechanical properties of fabric are affected by this process. Finally, it is pointed out that the relationship between concentration and weight reduction is not linear. The negative points mention in the study is decrease in tensile, tear for fabrics and yarn tensile strength. The effect of alkaline hydrolysis on bulk properties like drape, handle and touch has revealed that the hydrolysis is limited to the polyester surface with generation of some oligomers. The AFM images taken in this study to see the effect of alkaline hydrolysis is depicted in figure 4 [19].



(a) (b)

Figure 4. (a)Atomic force microscopy image of untreated polyester fiber. (b) Atomic force microscopy image (AFM) of alkali treated polyester fiber

3.4 Moisture transmission through fabric

Fabrics are the textile porous media made up of textile fibers in different textile forms. The interstices between the fibers provide the path for the transportation of moisture through the fabric. There mechanisms of moisture conduction through the textile fabric are as follows [35];

i) Adsorption (interaction of water on fabric surface)
ii) Absorption/diffusion (penetration through fabric interstices)
iii) Wicking (movement of water through fabric pores)
iv) Desorption/evaporation (water conduction to atmosphere)

The fiber, yarn and the fabric properties decide that which of the above mechanism dominate during the movement of water vapors through the fabric. Water vapors pass through a fabric in many different ways such as diffusion, absorption, desorption of water vapors and forced convection. The water transport mechanism is depicted in figure. Transport of moisture in a dry fabric takes place in 3 phases [36]:

a) Diffusion of water vapor and liquid water in the inter fiber voids replacing the air with liquid (it is mainly due to concentration gradient across the two surfaces). It is a fast process.
b) Moisture sorption into the fibers (it is slow process)
c) Stabilization state at which sorption, desorption, evaporation and condensation reach a steady state.

Heavy perspiration results in an increased amount of moisture, which can no longer be absorbed by the fibers. Instead, textiles worn close to the skin focus on mechanisms of “adsorption and migration” – the accumulation and removal of water vapor on and along the fibers. Here, sweat moves to the outer layer of the fabric where it can dissipate into the ambient air [37]. Different fabric types can be used to achieve this. One way is for the fabric to undergo chemical treatment, which increases the speed of moisture transfer to the outer threads. The movement of moisture from skin to the fabric and outer surface is depicted in figure 5 [37, 38].

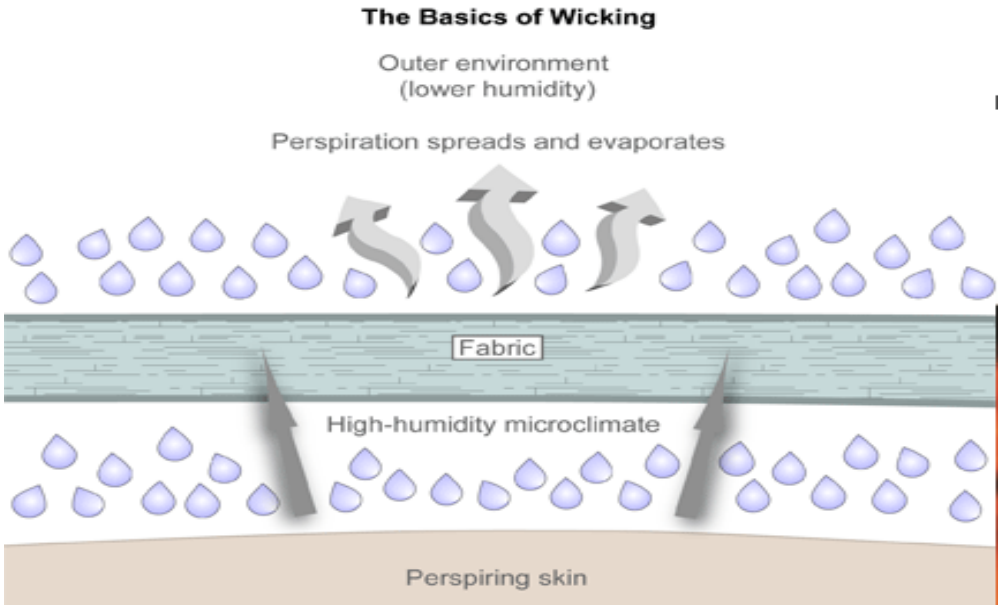


Figure 5. The wicking of moisture from human skin

3.4.1 Absorption/Diffusion

The interaction of liquids with textile have some fundamental physical phenomena: wetting of the fiber surface, transport of the liquid into assemblies of fibers, adsorption of the fiber surface, and diffusion of the liquid into the interior of the material [38].

The water vapor that is to move in a fibrous medium, it must wet the fiber surfaces before being transported through the interfiber pores by means of capillary action. The molecules on the surface of a liquid experience an imbalance of forces. Hence, there is presence of free energy at the surface of the liquid. The excess energy is called 'surface free energy', for a liquid to wet a solid completely, or for the solid to be submerged in a liquid, the solid surfaces must have sufficient surface energy to overcome the free surface energy of the liquid. The surface free energy can be quantified as a measurement of energy per area. It is usually termed 'surface tension' and is quantified as force per length, with units' mN/m or dynes/cm.

3.4.2 Fick's law of diffusion

Wettability of textiles depends upon chemical nature of fibers, the geometry of textiles and fibers, fiber diameter and fabric pore size. Physical properties of liquid such as surface tension, viscosity and density also determine its wetting and diffusion into the fabric surface. The water vapor diffusion through the textile fabric based upon the Fick's law can be expressed as:

$$J_A = -D_{AB} \nabla_{CA} \quad (2)$$

In two or more dimensions the use of ∇, the del or gradient operator, generalizes the first derivative. For diffusion only in one direction i.e. z direction the Fick rate equation is [39]:

$$J_{A,Z} = -D_{AB} \frac{dc_A}{dz} \quad (3)$$

Where $J_{A,z}$ is the molar flux in the z direction relative to the molar-average velocity, dc_A/dz is the concentration gradient in the z direction, and D_{AB}, the proportionality factor, is the mass diffusivity or diffusion coefficient for component A diffusing through component B. The negative sign indicates that J is positive when movement is down the gradient as towards region of low concentration. The dimensions of diffusion co-efficient are [length^2/time] i.e. (m^2/sec).

A more general flux relation that is not restricted to isothermal, isobaric systems was proposed by de Groot is expressed in equation 4:

$$\text{flux} = -\begin{pmatrix}\text{overall}\\ \text{density}\end{pmatrix}\begin{pmatrix}\text{diffusion}\\ \text{coefficient}\end{pmatrix}\begin{pmatrix}\text{concentration}\\ \text{gradient}\end{pmatrix}$$

$$J_{A,Z} = -cD_{AB} \frac{dy_A}{dz} \quad (4)$$

As the total concentration c is constant under isothermal, isobaric conditions, the above equation is a special form of the more general relation. An equivalent expression for $J_{A,z}$, the mass flux in the z direction relative to the mass-average velocity, is

$$J_{A,Z} = -D_{AB} \frac{d\rho_A}{dz} \quad (5)$$

Initial experimental investigations of molecular diffusion were unable to verify Fick's law of diffusion. This was apparently due to the fact that mass is often transferred simultaneously by two possible means: (i) as a result of the concentration differences as postulated by Fick and (ii) by convection differences induced by the density differences that resulted from the concentration variation. The liquid diffusivity into the porous textiles can be determined by the model derived by Li and Zhu [35] and it was evident from this model that during liquid moisture diffusion the temperature initially increases and then decreases and reaches an equilibrium value. This may be related to the heat of sorption produced when liquid starts to diffuse into fabric. The amount of heat is greater for fibers with higher hygroscopic character.

3.4.3 Transient water transport in woven fabrics

Moisture transport through the fabric is generally not related to the steady state conditions because under actual wearing conditions there is inherent variability in the amount of moisture released, atmospheric conditions, and body motion and positioning. The major mechanism of moisture transfer through the clothing at low moisture contents is vapor diffusion; Wicking between fabrics does not take place until there is a sufficient amount of water to fill capillaries that are formed between fibers and yarns. This critical amount of moisture is well above the maximum absorption capacity of the fibers. In the case of 100% woven cotton fabric, wicking does not begin until the moisture content is close to 110% above regain, while maximum fabric absorption capacity is close to 30% above regain. Polyester fabric with hydrophilic finish to promote wicking does have improved wicking rates compared to conventional polyester, but does not have improved moisture transport at low moisture contents [40].

The change in concentration of the liquid with time during diffusion can be predicted through Fick's second law of diffusion [41]:

$$\frac{\partial \emptyset}{\partial t} = D \ \frac{\partial^2 \emptyset}{\partial x^2} \tag{6}$$

Where φ the concentration in dimensions of (amount of substance/length^3), t is time in sec, D is the diffusion co-efficient in dimensions of (m^2/sec) and x is the length in m. A study [42] has conducted on the water transport through different woven hygroscopic and hydrophobic fabrics and it is concluded that Transient transport of liquid water along a woven fabric appears to follow a non-Fick effect within a limited space and in a very short time. After this transient period the water follows the classical mass diffusivity theory as proposed by Fick's law. According to this study the higher the hydrophobicity of the fabric the higher, higher the transport velocity of liquid in the fabric and more will be the non-Fick effect.

The moisture diffusivity of a textile material is influenced by a number of factors;

a) It decreases with an increase in the fiber volume fraction of the material.
b) The moisture diffusivity through the fabric decreases with an increase in the flatness of the fiber cross section [43].

c) The increase in fabric thickness reduces the porosity of the material thus diffusion rate is reduced. Water vapor diffusion is highly dependent on the air permeability of the fabric [44].

d) The type of finish applied (i.e. hydrophilic or hydrophobic) to a fabric has no great effect on the diffusion process [45].

The diffusion co-efficient of water vapor in air can be given as a function of temperature and pressure by the following equation [46]:

$$D = 2.20 \times 10^{-5} \left(\frac{\theta}{\theta_0}\right)^2 \left(\frac{P_0}{P}\right) \quad (7)$$

Where D is the diffusion co-efficient of water vapor in air (m^2/sec), θ is the absolute temperature (K), θ_o is the standard temperature of 273.15 K, P is the atmospheric pressure and P_o is the standard pressure (Bar). In general, the diffusion co-efficient of fibers increases with an increase in the concentration of water in the fibers; an exception to this behavior is shown by polypropylene [15], due to its high hydrophobicity. The water vapor transmission through fabrics increases with an increase in the moisture content and in the condensation of water in the fabric.

3.4.4 Liquid water transmission/Wicking

The flow of liquid moisture through textiles is caused by fiber-liquid molecular attraction at the surface of the fibrous materials, which is mainly determined by the surface tension and the effective capillary pore distribution and pathways[14]. Liquid transfer through a porous structure involves two sequential processes – wetting and wicking. Wetting is the initial process involved in fluid spreading. Wicking starts as soon as the area in contact with water becomes saturated. In sweating conditions, wicking is the most effective process to maintain a feel of comfort. The clothing with high wicking properties spreads moisture coming from the skin throughout the fabric offering a dry feeling and the spreading of the liquid enables moisture to evaporate easily [47].

When the liquid wets the fibers, it reaches the spaces between the fibers and produces a capillary pressure. The liquid is forced by this pressure and is dragged along the capillary due to the curvature of the meniscus in the narrow confines of the pores as shown in the Figure 6 [37].

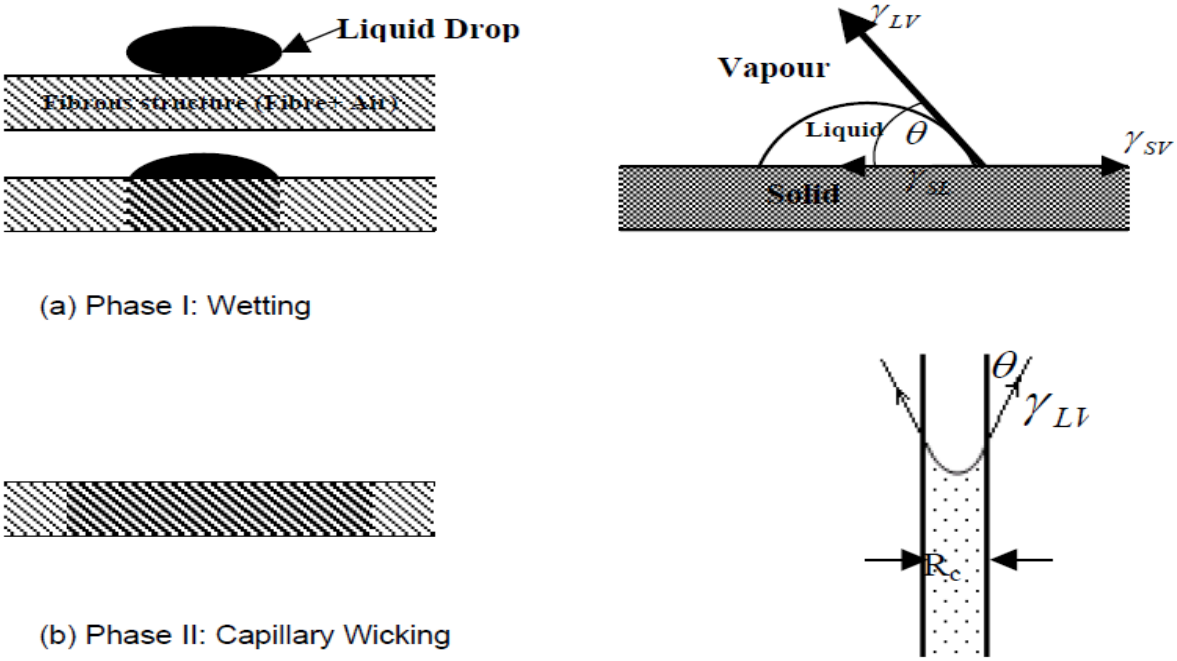


Figure 6. Moisture transfer process through porous media

The magnitude of the capillary pressure [48] is given by the Laplace equation:

$$P = \frac{2\,\gamma_{LV}\,cos\theta}{R_c} \tag{8}$$

Where P is the capillary pressure developed in a capillary tube of radius Rc . A difference in the capillary pressure in the pores is the reason for spreading of fluid in the given media. Hence, a liquid that does not wet the fibers cannot wick into the fabric [49]. The ability to sustain the capillary flow is known as wickability of material. The distance travelled by a liquid flowing under capillary pressure, in horizontal capillaries, is approximately given by the Washburn-Lukas equation [50]:

$$L = \sqrt{\frac{R_c \gamma cos\theta}{2\eta}\,t} \tag{9}$$

Where, L is the capillary rise of the liquid in time t and η is the viscosity of the liquid. The amount of water that wicks through the channel is directly proportional to the pressure gradient. When a dry porous medium, such as a fabric etc. is brought into contact with a liquid, it will start absorbing the liquid at a rate which decreases over time. For a bar of material with cross-sectional area A that is wetted on one end, the cumulative volume V of absorbed liquid after a time t is:

$$V = AS\sqrt{t} \quad (10)$$

Water vapor transmission of quick dry fabrics with warp of a normal draw textured yarn and weft of microporous polyester yarns has been determined by Wang and co-workers [51]. They have made a conclusion that the wicking area decreased with time i-e wicking speed become slower over time. Additive treatment is found to have no effect on wicking area. Cover factor is found inversely proportional to wicking. Hydrophilic additives are found to enhance the vapor transmission property; silicon softeners were found to reduce the "quick dry property".

The validity of Washburn equation for wicking kinetics has been examined by Zhaung and co-workers using an automatic image analysis technique [52]. The technique is used to analyze the vertical and horizontal wicking of different types of knitted fabrics that are usually worn next to skin. It has been found that the Washburn equation is obeyed quite well for horizontal wicking while for vertical wicking it is valid only when saturated and unsaturated zones are accounted separately. A saturated and unsaturated zone is also defined according to the absorption behavior of the fabric.

3.4.5 Desorption/Evaporation

Evaporation from a textile takes place due to temperature and moisture distribution. Evaporation and sorption can take place simultaneously during capillary action of a liquid. The desorption and evaporation from a fabric depend manly on hydrophilicity of fibers, the yarn and fabric structure. Higher the proportion of hydrophilic fibers the lower will be the evaporation due moisture binding in the hydrophilic fibers. During capillary action evaporation and sorption takes place at the same time. The drying rate of micro denier knitted fabrics is higher than that of normal denier yarn [53]. Also micro denier fibers have greater holding capacity due to greater surface area and thus they have increased moisture transmission capacity.

If evaporation takes place in an enclosed area, the escaping molecules accumulate as a vapor above the liquid. Many of the molecules return to the liquid, with returning molecules becoming more frequent as the density and pressure of the vapor increases. When the process of escape and return reaches an equilibrium the vapor is said to be "saturated," and no further change in vapor pressure and density or liquid temperature will occur [54]. For a system consisting of vapor and liquid of a

pure substance, this equilibrium state is directly related to the vapor pressure of the substance, as given by the Clausius-Clapeyron relation:

$$ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (11)$$

Where P1, P2 are the vapor pressures at temperatures T_1, T_2 respectively, ΔHvap is the enthalpy of vaporization, and R is the universal gas constant. The rate of evaporation in an open system is related to the vapor pressure found in a closed system. If a liquid is heated, the liquid will boil, when the vapor pressure reaches the ambient pressure.

The dynamic surface wetness of fabrics, as described by Scheurell and co-researchers [55], is an important parameter influencing the skin contact comfort in actual wear, as it is influenced by both the collection and the passage of moisture along the fabric. The dynamic surface wetness of fabrics has been found to correlate with the skin contact comfort in wear for a variety of types of fabrics, suggesting that the mobility of thin films of condensed moisture is an important element of wearing comfort.

3.5 Effects of Laundry on fabrics

Washing process of textiles is carried out during service and it is regulated by chemistry, mechanical agitation, temperature and time. The impact of particular factors can be represented by a washing cycle and its parameters within which is the circle dealing with water that combinely connects the factors in the process. The components of washing, detergent and their synergic effect determines the chemical activity and its efficacy. One of the primary requirements for a successful detergent formulation is to remove various soils and preserve an initial characteristic of textile materials as long as possible. Surfactants play an important and double role in the soil removal: it has the tendency to overcome the attraction between soil and fabric by attaching themselves to both, loosen the soil and deflocculates it at the same time, i.e. they break it up into colloidal particles and stabilize their aqueous dispersion. The presence of anionic and non-ionic surfactants in the washing bath has enhanced the effect of deflocculation and soil removal efficiency. The development of new detergent formulations is targeted to low temperature washing based mostly, on the high efficient and environmental friendly components [56, 57].

Soil removal during washing process is also enhanced by mechanical input, proper wash time and temperature [58]. Synergy of all mentioned factors impact on changes of textiles occurred in

washing. The quality of water is a key parameter, thus in some cases the cumulative effect of frequent washing can be high inorganic and organic matters content on the textiles. The accumulation of deposits can cause negative effects, e.g. harsh and stiff hand, progress in degradation and tearing, as well as reduced usability of the textiles. Textiles subjected to the mostly aggressive chemicals, mechanical agitation superimposed by high temperature and duration during washing is capable to cause damage after frequent washing. It is known that washing affects generally more to fabric damage than the usage or wear [59].

The frequent washing cycles can cause the fiber surface modification as result of fiber swelling capacity in the alkaline detergent bath superimposed by mechanical agitation. Cellulose textiles are exposed to a swelling in an alkali medium, which brings changes in pore structure, tendency to fibrillation and surface changes. Fibers surface charge is important parameter in the wet processing of cotton. Electro kinetic properties of the fiber are possible to characterize with a double layer model created at the interface fiber/electrolyte solution [60]. Electro kinetic double layer is characterized by zeta potential which depends on the nature of fiber functional groups, type and the number of the dissociating groups, hydrophilicity, as well as ion and water sorption from the solution accordingly. Most textile fibers possess negative charge in neutral aqueous solutions. The zeta potential on a material's surface in contact with a polar medium, is governed by the dissociation of surface groups, the preferential adsorption of cations or anions, the adsorption of polyelectrolytes and surfactants, the isomorphic substitution of cations and anions, and the accumulation or depletion of electrons. It provides insight into the charge and adsorption characteristics of solid surfaces [61].

3.6 Hydrophilic surfaces

As hydrophilic surface can be defined as surface that "attracts water" and the water contact angle should be smaller than 90°. For a liquid to wet a solid completely, or for the solid to be submerged in a liquid, the solid surfaces must have sufficient surface energy to overcome the free surface energy of the liquid. The surface free energy can be quantified as a measurement of energy per area. Three interfaces come into play if a liquid drop is deposited on a solid surface, and three interfacial tensions are involved: γ_{sv}, γ_{sl}, γ_{lv}, respectively the solid–vapor, solid–liquid, and liquid–vapor interfacial tensions. The force involved when the water vapor interacts with the solid or fabric surface is given by Young-Dupree equation [15],

$$\gamma_L \cos\theta = \gamma_s + \gamma_{SL} \quad (12)$$

where γ represents the interfacial tension that exists between the various combinations of solid, liquid, and vapor; the subscripts *S*, *L*, and *V* standing for solid, liquid, and vapor, and θ is the equilibrium contact angle as depicted in figure 6. Surface roughness is necessary feature of superhydrophobicity and superhydrophilicity, the principles of these phenomena are deeply explained by Wenzel and Cassie and Baxter who described contact angles and different mechanisms of wetting on rough surfaces.

3.6.1 Hydrophilicity of solid surfaces

It is of great fundamental and practical interest to know how the contact angle depends on the chemical composition of both the solid and the liquid. The solids can be divided in two main types depending on the strength of bonding within the molecular structure: compact solids (covalent, ionic, or metallic), and weak molecular solids (van der Waals forces and hydrogen bonds). The different binding forces that vary in these materials leads to the surface free energy at the solid–vacuum interface to be very different and is a fundamental parameter of a solid. This difference in surface free energy have the tendency for solid surfaces to show different kinds of wetting behavior when brought into contact with a liquid. The detailed wetting behavior is determined by Young's equation 12. The relation between the three interfacial tensions have enabled us to conclude that by using γ_{sv} and γ_{lv} can roughly predict the wetting behavior. For a liquid with $\gamma_{lv} < \gamma_{sv}$, the total free energy would in general be minimized by maximizing the area of the liquid–vapor interface, and the liquid would wet the solid. However, if a liquid has $\gamma_{lv} > \gamma_{sv}$, the total free energy would in general be minimized by minimizing the area of the liquid–vapor interface and the liquid would partially wet the solid. Therefore, knowledge of γ_{sv} for a particular solid surface provides a means that we can look into the insight of wetting behavior of liquids on that surface [62].

3.6.2 Surface free energy (Critical surface tension)

The pioneering work goes back to Zisman. The observations made by Zisman and his coworkers was that for a given solid, the measured contact angles did not vary randomly as the liquid was varied. Based on Young's equation (12) different approaches have been developed to determine the solid surface tension. The main hurdle in this measurement is that Young's equation contains two non-measurable quantities, γ_{sv} and γ_{sl}, that cannot be measured independently. The strategy

conducted by all approaches is to express γ_{sl} in terms of the other two interfacial tensions, $\gamma sl = f(\gamma_{sv}, \gamma_{lv})$, reducing the number of unknowns in the Young equation. Thus, the interfacial tension which is caused by the interaction between solid and liquid molecules has to be calculated from the knowledge of the surface properties of the solid and of the liquid phase. The available models are empirically modified or there must be some theoretically sound approximations.

3.6.3 Critical surface tension (Geometric mean combining method)

One such approximation that has proved to be very stimulating to research on contact angle phenomena was proposed by Girifalco and Good assuming that mainly van der Waals forces act between all molecules [63]. It is based on Berthelot's (geometric mean) combining rule. According to this rule the free energy of adhesion W_{sl}^{a} can be approximated in terms of the free energy of cohesion of the solid, W_{ss}^{c}, and the free energy of cohesion of the liquid, W_{ll}^{c}. Girifalco and Good modified the geometric mean combining rule by introducing an empirical correction factor called interaction parameter Φ.

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\,\Phi\sqrt{\gamma_{sv}\gamma_{lv}} \qquad (13)$$

This interaction parameter Φ is a characteristic of a given system that can be evaluated from molecular properties of the solid and the liquid phase. It was found to be very close to unity when dominant cohesive and adhesive forces were of the same kind.

3.6.4 Critical surface tension (Equation of state approach)

Based on experimental contact angle data, Neumann and coworkers have shown that the values of $\gamma_{lv}\cos\theta$ change systematically with γ_{lv} in a very regular fashion, from hydrophobic surfaces, such as polytetrafluoroethylene, to hydrophilic surfaces, such as poly(propene-alt-N-methylmaleimide), and that the patterns are independent of the experimental technique [64] as shown in figure 7.It can be concluded that the values of $\gamma_{lv}\cos\theta$ depend only on γlv and γsv, i. e. $\gamma_{lv}\cos\theta$ is a function of γ_{lv} and γ_{sv}:

$$\gamma_{lv}cos\theta = F\,(\gamma_{lv}\,\gamma_{sv}) \qquad (14)$$

Because of Young's equation (12), the experimental contact angles leads to the approximation that γ_{sl} can be expressed as a function of only γ_{lv} and γ_{sv}:

$$\gamma_{sl} = F\,(\,\gamma_{lv}\,\gamma_{sv}) \tag{15}$$

These experimental results are considered to be related with the equation of state approach for interfacial tensions [65]: A modified formulation of the equation-of-state can be written as

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sv}\gamma_{Lv}}\, e^{-\beta\,(\gamma_{lv}-\gamma_{sv})2} \tag{16}$$

The young equation can be combined with the relation obtained in equation 16.

$$Cos\,\theta = -1 + \sqrt{\frac{\gamma_{sv}}{\gamma_{lv}}}\, e^{-\beta\,(\gamma_{lv}-\gamma_{sv})2} \tag{17}$$

Thus, the solid surface tension can be determined from experimental contact angles and liquid surface tensions when β is known. β was determined experimentally for a given set of γ_{lv} and θ data measured on one and the same type of solid surface by least-squares analysis technique.

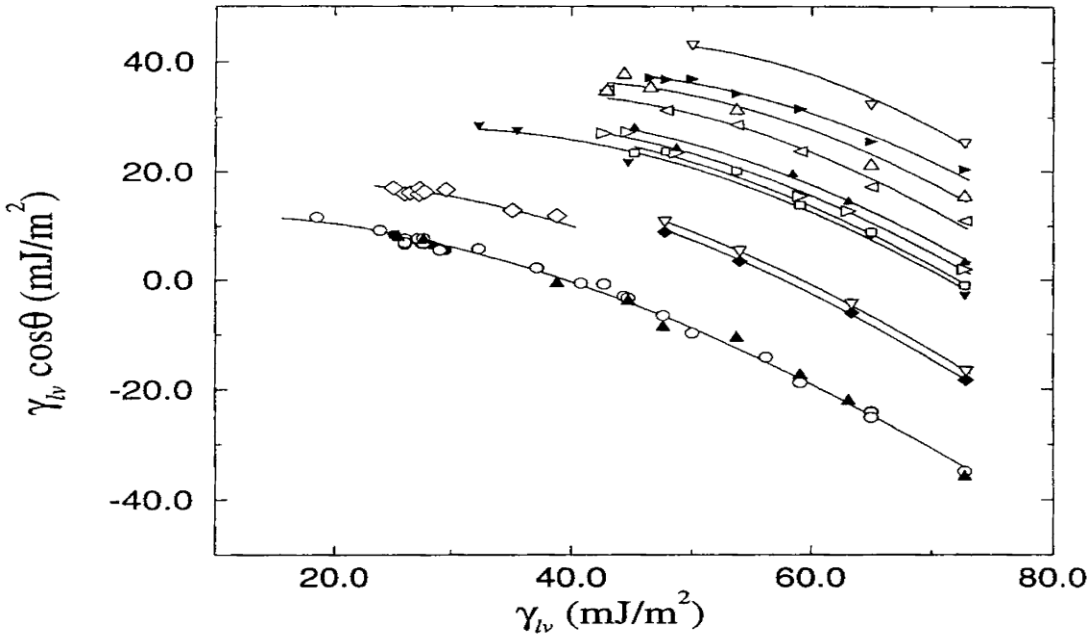


Figure 7. Plots of γlvcosθ vs. γlv for various solid polymer surfaces [64]

●	FC-721-coated mica
○	FC-722-coated mica and wafer
▲	FC-725-coated wafer
◇	Teflon FEP
◆	hexatriacontane
▽	cholesteryl acetate
▼	poly(propene-*alt*-*N*-(*n*-hexyl)maleimide)
□	poly(*n*-butyl methacrylate)
▷	polystyrene
▲	poly(styrene-(hexyl/10-carboxydecyl 90:10)-maleimide)
◁	poly(methyl methacrylate/*n*-butyl methacrylate)
△	poly(propene-*alt*-*N*-(*n*-propyl)maleimide)
►	poly(methyl methacrylate)
▽	poly(propene-*alt*-*N*-methylmaleimide)

Figure 8. Legend for the graph in figure 7

Recently, van Giessen, Bukman and Widom used a generalized van der Waals theory to model a diverse series of liquids on a low-energy substrate and to calculate the corresponding surface tensions and contact angles. The aim of this study was to investigate how the behavior of cosθ with γlv is related to molecular interactions [66]. Their results showed that it was indeed possible to reproduce behavior similar to that seen in experiments (figure 7), with the data for cosθ plotted versus γlv falling in a narrow band which could almost be interpreted as a smooth curve. In their calculation, the width of the band depended on the ranges of the model parameters and on the details of the molecular structure. The main limitations of their model were its simplicity and the fact that they had to use a combining rule to estimate the interaction between the solid and the fluid. Several other approaches have been developed to calculate the solid–vapour surface tension from contact angle measurements [67].

3.6.5 Critical surface tension (Combining surface tension components)

The surface tension component approach has been established by Fowkes. He postulated that the total surface tension can be expressed as a sum of different surface tension components. Each of the component arises due to a specific type of intermolecular forces. The relation obtained by Fowkes is expressed in equation 18,

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sv}^{d}\gamma_{lv}^{d}} \qquad (18)$$

Where γ_{sv}^{d} and γ_{lv}^{d} are the dispersion force components of the solid and liquid surface tension respectively. Owens and Wendt and others has worked on it in order to reach the conclusion that the "polar" interaction could be computed using the same geometric mean mixing rule as for the dispersion force interaction [68].

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sv}^{d}\gamma_{lv}^{d}} - 2\sqrt{\gamma_{sv}^{p}\gamma_{lv}^{p}} \quad (19)$$

Where γ_{sv}^{p} and γ_{lv}^{p} are the polar force components of the solid and liquid surface tension. If the contact angles of at least two liquids, usually a polar and a nonpolar liquid, with known γ_{lv}^{d} and γ_{sv}^{d} parameters are measured on a solid surface, the γsv d and γsv p parameters of that solid can be calculated by combining equation 19 with the Young equation 12. The theoretical background of this approach is based on especially, assumption that the polar component of the surface tension can be calculated by a geometric mean combining rule from the internal polar cohesive forces. It can easily be proved that different sets of probe liquids lead to different polarity splits for a given solid.

3.7 Methods to Produce Hydrophilic Surfaces

The enhancement of hydrophilicity of surfaces can be attained through either deposition of a molecular or microscopic film of a new material, more hydrophilic than the substrate, or by modification of chemistry of the substrate surface. Molecular modification or deposition of coating is more common choice for inorganic substrates whereas modification of surface chemistry is broadly used in the case of polymeric materials.

3.7.1 Modification of surface chemistry

Over the last few decades, many advances have been made in developing surface treatments by plasma, corona, flame, photons, electrons, ions, X-rays, gamma-rays, and ozone to alter the chemistry of polymer surfaces without affecting their bulk properties. Plasma treatment [69], in air or oxygen environment, corona and flame treatments are the most designated techniques in oxidation of surfaces of polymers. In both plasma and corona treatments, the accelerated electrons bombard the polymer with energies 2-3 times that necessary to break the molecular bonds, producing free radicals which generate cross-linking and react with surrounding oxygen to produce oxygen-based functionalities [70]. Polar groups being typically created on the surface are

hydroxyl, peroxy, carbonyl, carbonate, ether, ester, and carboxylic acid groups [71]. In flame treatment, surface combustion of polymer takes place with formation of hydroperoxide and hydroxyl radicals. Oxidation depth through flame treatment is around 510 nm, and over 10 nm for air plasma treatment [72]. Plasma, corona and flame treatments end in extensive surface oxidation and results in highly wettable surfaces. Polar groups produced during surface oxidation have tendency to be buried away in the bulk when in contact with air for extended period of time, but they remain on the surface when in contact with water or any other polar environment.

Alkali treatment of polymers, especially at elevated temperature, can also enhance surface hydrophilicity of polymers. Hydroxyl and carboxyl groups are among the hydrophilic groups formed on the surface of polymers such as polyolefins and polyethylene terephthalate during their etching with concentrated bases [25]. The hydrophilic surface must be kept free of contaminants such as airborne organics, moisture and dust particles to preserve its wetting characteristics. A freshly prepared hydrophilic surface when exposed to the laboratory environment tends to achieve its lowest energy (most stable state) by instantaneous changes at the surface, e.g., adsorption of water molecules or organic contaminants. In this way, contamination of hydrophilic surface and consequently a reduction of surface energy occur naturally for many materials.

3.7.2 Deposited molecular structures

A number of organic molecules adsorb from either solution or a vapor phase on selected solids, spontaneously organize into self-assembled monolayers, changing wetting characteristics of the substrate [73]. The most commonly studied densely packed molecular structures include silicon [74], aluminium [75], titanium and other oxides [76]. Deposited organic layers make the surface hydrophilic if the end group is polar, other than saturated hydrocarbon-based group or fluorinated group. The highest hydrophilicity are probably the groups capable of interacting with water molecules through hydrogen bonding such as -OH, -COOH. Both mono- and multi-layers can also be deposited mechanically through a different techniques. Physically deposited multilayers are prone to poor stability when contacted with liquids.

3.8 Applications of wetting and hydrophilic polymeric surfaces

3.8.1 Fogging resistant surfaces

The anti-fogging surfaces gain importance in response to encounter the visualization under high humidity. Swimming goggle is a most obvious example for application. Since the relative humidity is a strong function of temperature, the vapor can easily reach its saturation limit due to the temperature fluctuation or at a relatively cold solid surface, such as, the lenses or transparent walls to see through. As a result, significant condensation in form of tiny droplets can be induced. The originally transparent solid surfaces will then fog and lose their optical clarity. A hydrophilic surface can be anti-fog because water spreads on the rough hydrophilic surface to form a thin film instead of droplets. Such an effect can be easily demonstrated by placing a piece of hydrophilic polyester film on top of a cup filled with hot water. The plasma-treated superhydrophilic polyester film remained clear due to the formation of a continuous water film [77].

3.8.2 Biomedical applications

Hydrophilic coatings have been used in the medical field for the last few decades, for example in catheters, guide wires, and other vascular access devices for fertility, contraception, endoscopy, and respiratory care. Polyvinylpyrolidone, polyurethanes, polyacrylic acid, polyethylene oxide, and polysaccharides were the main polymeric components in hydrophilic coatings [78]. Reduction in friction is the need in design of hydrophilic coatings. Recently, these coatings are also moving toward anti-fouling, antimicrobial and/or biologically active surfaces that perform tasks other than imparting lubricity. Also superhydrophilic coatings attracted interest among biomedical engineering research teams. Flat surfaces with strong affinity to water can be used for improving biocompatibility and affinity to water of implant materials. Contact lenses are developed in the field of vision correction from highly oxygen permeable silicone hydrogels that fulfil the metabolic needs of the cornea, maintain its physiological health, and can be worn continuously for several days [79]. The high biocompatibility, elastic modulus that closely matches human bone, good ductility, fatigue and tensile strength, makes titanium (Ti) and Ti-based alloys very popular for orthopedic implants [78, 80].

3.8.3 Other applications

Many other applications of hydrophilic and superhydrophilic surfaces have been known. Hydrophilic modification of polyester has been widely done in order to have an effective way to improve adhesion. Surfaces that has the tendency to exhibit tunable wettability from superhydrophilic to superhydrophobic, especially that are coated and applied with conductive polymers [81] or nanomaterials, such as ZnO nanorods [82], carbon nanotubes and graphene [83]. More applications of the hydrophilic surfaces are under consideration and will be in market in near future.

CHAPTER 4
MATERIALS AND METHODS

4.1 Materials

The fabric used in this study was lab grade 100 % polyester with GSM 165 with equal warp and weft density of 20 threads per cm. The fabric was treated with hot water in order to remove any wax and dirt. Laboratory grade caustic soda flakes were used for caustic treatment of the samples and laboratory grade acetic acid was used to neutralize the fabric after the caustic treatment. Lab grade Glycerin and urea is obtained from Sigma Aldrich.

Commercial polyester film of 30 µm in thickness is selected. The film is Mylar^{TM,} supplied by DUPONT. The selected material has good properties high melting temperature (> 250 ˚C), good mechanical strength, plasticity and intrinsic low surface energy makes it a potential material for chemical surface modification. Caustic soda flakes, ethyl alcohol, acetic acid and sulphuric acid of highest purity are obtained from Sigma Aldrich and used as received.

4.2 Methodology

4.2.1 Alkali Surface hydrophilization of polyester fabric

Polyester samples were impregnated in caustic soda solution (20 g/l and 50 g/l) at two concentrations and then padded at the pickup of 80%. The experiments are conducted, one to see the effect of concentration, time and temperature of treatment. The schematic diagram of the method for conduction of experiments is shown in figure 7. Second set of experiments are conducted with the addition of 50 g/l urea with 50 g/l NaOH at 150 °C for different times. Standard treatment (NaOH 50 g/l, time 30 minutes and temperature at 90 °C) is also done for comparison. The glycerin treatment is also carried out by pad dry method in the similar way as the sodium hydroxide treatment is done. The technique used for alkali treatment is the impregnation of polyester fabric in padding bath and then drying under tension state at fixed width. The purpose of fixing the width of fabric is to minimize the effect of shrinkage that can occur during high temperature hot drying. After padding and drying the fabric samples were rinsed and neutralized with acetic acid until all the caustic soda is removed from the samples. All the treated samples were dried in ambient air followed by conditioning and testing.

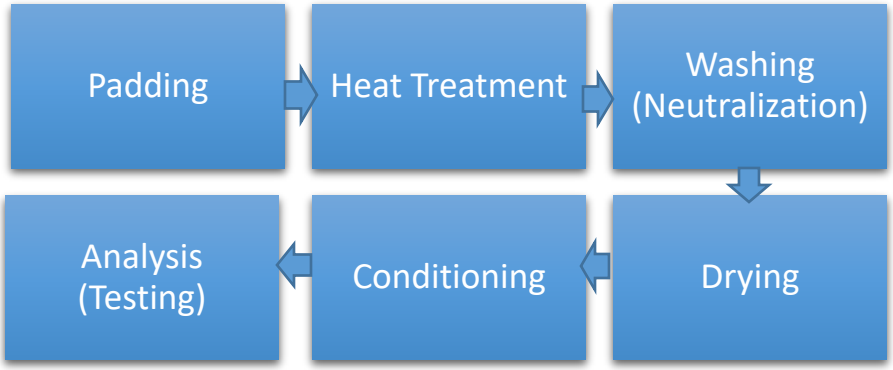


Figure 9. Scheme of treatment for polyester fabric

4.2.2 Ozone treatment

Ozone gas treatment was carried out on the equipment as shown in figure 8 for 60 minutes at atmospheric pressure [84].

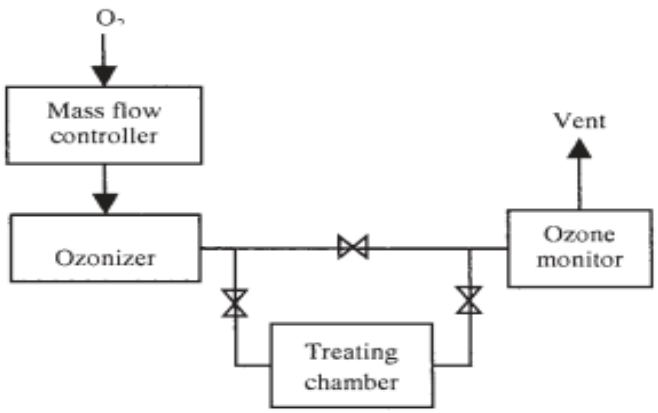


Figure 10. Flow chart for ozone gas treatment

4.2.3 Plasma treatment

Atmospheric pressure plasma (APP) treatment was performed using plasma pre-treatment equipment (Diener electronic, Germany) with compressed air as a reactive gas source. APP was generated by means of high-voltage discharge inside the nozzle jet coupled to the stepped high-frequency pulse current power supply (plasma generator) through the high-voltage transformer. The plasma processing parameters used were as described by Gotoh et al [85]. The distance between the nozzle and the horizontally set fabric was 8mm. The polyester fabric, moving at

0.2m/s, was exposed to the plasma jet, diameter 20 mm. The treatment was carried out twice. Both sides of the polyester fabric were exposed to the plasma jet.

4.3 Optimization of treatment parameters for alkali Hydrophilized polyester

The polyester fabric is first treated with non-ionic detergent followed by hot water in order to remove any dirt, dust and wax. The fabric was then dried, stabilized and conditioned. The sodium hydroxide treatment effect is studied under three variables.

- Sodium Hydroxide Concentration (SHC)
- Time of Treatment (TIME)
- Temperature for treatment (TEMP)

Three levels of sodium hydroxide concentration are selected that are 20 g/l, 35 g/l and 50 g/l. Three different levels of treatment time (2, 4 and 6 minutes) and three different levels of treatment temperature (130 ˚C, 150 ˚C and 170 ˚C). The optimization was performed using Box-Behnken design and response surface modeling under three levels and three factors as mentioned in table 1. The mathematical relationship between the three independent variables and the response is approximated by the second order polynomial as given in equation (20) and equation (21).

Table 1. Selected factors and levels for sodium hydroxide treatment of polyester fabric

Number of Factors	Levels		
	[-]	[0]	[+]
SHC (g/l)	20	35	50
TIME (min)	2	4	6
TEMP (˚C)	130	150	170

$$\boldsymbol{Percentage\ weight\ loss} = X_0 - X_1.SHC - X_2.TIME + X_3.TEMP + X_{11}.SHC^2 - X_{22}.TIME^2 - X_{33}.\ TEMP^2 + X_{12}.SHC.TIME + X_{13}.SHC.TEMP + X_{23}.TIME.TEMP \quad (20)$$

$$\boldsymbol{Vertical\ Wicking} = -Y_0 + Y_1.SHC + Y_2.TIME + Y_3.TEMP - Y_{11}.SHC^2 + Y_{22}.TIME^2 - Y_{33}.\ TEMP^2 + Y_{12}.SHC.TIME + Y_{13}.SHC.TEMP - Y_{23}.TIME.TEMP \quad (21)$$

Where X_0 and Y_0 are model constant; X_1, X_2, X_3 and Y_1, Y_2, Y_3 are linear coefficients; X_{12}, X_{13}, $X_{23}$and Y_{12}, Y_{13}, Y_{23} are cross product coefficients and X_{11}, X_{22} , X_{33} and Y_{11}, Y_{22}, Y_{33} are the quadratic coefficients. The coefficients of main effect and two factor interaction effect are estimated from the experimental results using the mathematical software package MINITAB.

4.4 Characterization of Hydrophilized Polyester fabric

4.4.1 Capillary rise measurements (Wicking)

The rise of liquid in the fabric is measured according to the AATCC 197 method. The samples were placed vertically with the lower end dipped in a thin layer of a 1 % solution of methylene blue dye that has no affinity towards synthetic fibers as shown in Figure 10. The apparatus was set in a closed chamber in order to keep a saturated vapor atmosphere. The blue coloration of dye solution on white fabric clearly indicated the height of capillary rise, and a ruler marked off in millimeters assembled along the fabric can make the height measurement easier. Height readings were recorded 20 minutes after the fabric was dipped in the liquid. Each measurement was carried out 5 times and the average height values were regarded as the final results.

The flow of liquid moisture through textiles is caused by fiber-liquid molecular attraction at the surface of the fibrous materials, which is mainly determined by the surface tension and the effective capillary pore distribution and pathways. Liquid transfer through a porous structure involves two sequential processes – wetting and wicking. Wetting is the initial process involved in fluid spreading. Wicking starts as soon as the area in contact with water becomes saturated. In sweating conditions, wicking is the most effective process to maintain a feel of comfort. The clothing with high wicking properties spreads moisture coming from the skin throughout the fabric offering a dry feeling and the spreading of the liquid enables moisture to evaporate easily [86]. When the liquid wets the fibers, it reaches the spaces between the fibers and produces a capillary pressure. The liquid is forced by this pressure and is dragged along the capillary due to the curvature of the meniscus in the narrow confines of the pores. The distance travelled by a liquid flowing under capillary pressure, in horizontal capillaries, is approximately given by the Washburn-Lukas equation:

$$L = \sqrt{\frac{R_c\,\gamma\cos\theta}{2\,\eta}\,t} \tag{22}$$

Where, L is the capillary rise of the liquid in time t and η is the viscosity of the liquid.

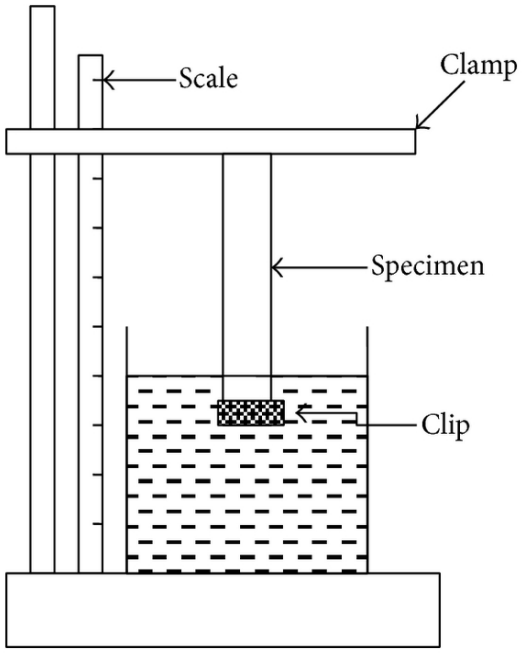


Figure 11. Schematic diagram for capillary rise measurements and mechanism

4.4.2 Percentage weight loss

The weight of the fabric samples that were treated with the alkali were measured before and after the treatments using an electronic balance with an accuracy level of ± 0.001 g and the percentage weight loss was calculated using the following formula:

$$Percentage\ weight\ loss = \frac{W1-W2}{W1}\ 100 \qquad (23)$$

Where W1 and W2 are weights of the fabric samples before and after the alkali treatment respectively.

4.4.3 X-Ray photoelectron spectroscopy (XPS) analysis

XPS is an extremely surface sensitive method allowing us to identify and quantify the chemical elements in the surface region of a solid and give information on the binding states of these elements, their oxidation numbers or functionalities. Soft X-Rays excite electrons from the inner shells or valence bands, which are ejected. The photoelectron spectrometer measures quantitatively the number of photoelectrons as a function of incident energy which are leaving the sample surface.

The energy spectrum is characteristic of the elemental composition and binding state of atoms at the sample surface. Therefore it can be used to quantitatively determine the surface composition of different species. XPS measurement is performed on machine by Omicron Technology. Monochromatic primary radiation is used. The measurement is done in CAE mode with constant pass energy for surveillance of 50 [eV] and 20 [eV] spectrum. It is done for detail measurement of individual line spectra.

XPS is an extremely surface sensitive method. The spectral information appears from a depth of approximately 10 nm in maximum. Of course X-Rays penetrate the depth of the sample. Everywhere where X-Ray quanta interact with electrons there is a probability to release electrons. The photoelectrons produced in the depth of the sample have a high probability to interact with other electron and dissipate their kinetic energy fully or partly. If these inelastically scattered photoelectrons leave the sample surface and are introduced into the spectrometer they do not give a contribution to the spectroscopic information because their kinetic energies are insignificant for their origin. They will be found in the spectrum's background. Otherwise, photoelectrons generated near the sample surface do not have a high probability to interact with other electron orbitals. Hence, their kinetic energy can be used to determine the binding energy and the counting of these photoelectrons contribute to the spectral information of the XPS spectrum.

4.5 Surface treatment of polyester film

The polyester film is immersed in alcohol water solution (1/1, v/v) for 2 hours in order to remove any dirt or oil for clean surface, rinsed with distilled water and then dried at room temperature for 24 hours. For hydrolysis reaction by acid the film is immersed in solution of sulphuric acid for specific time of treatment at room temperature. Two concentrations of sulphuric acid, 75 % and 80 %, are used for the treatment of film. The time of treatment for 80 % concentration of sulphuric acid is 3 sec and for 75 % concentration of sulphuric acid is 2 min. After this treatment the samples are rinsed and dried at room temperature for 12 hours. The acid treatment is followed by alkali treatment of samples at 90 ˚C and for time of treatment (30 sec, 1, 2, 4, 6…16min). Alkali treatment is followed by neutralization of samples by 5 % solution of acetic acid followed by rinsing and drying at room temperature overnight. All the samples are conditioned and then measurements are carried out. The schematic diagram of treatment of samples is shown in figure 11.

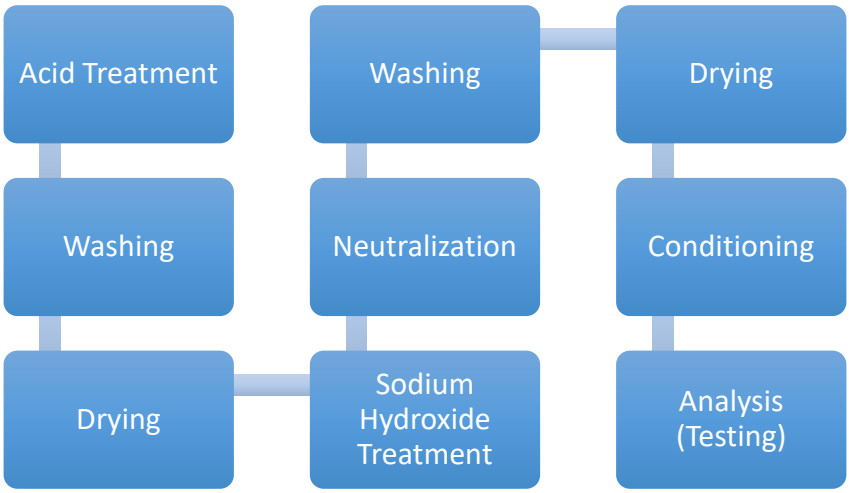


Figure 12. Scheme of treatment for polyester film

4.6 Characterization of polyester film

4.6.1 Contact angle measurements

The surface wettability is evaluated using the sessile drop method and measurements are carried out on Advex instrument (figure 12) using 5 µl for liquid drop contact angle measurements. This measurement is used both to assess the wettability of the polymer film and critical surface energy measurements. Each sample is measured 10 times for liquid at room temperature and the contact angle (CA) values are averaged. The averaged measurements are shown is table 2.

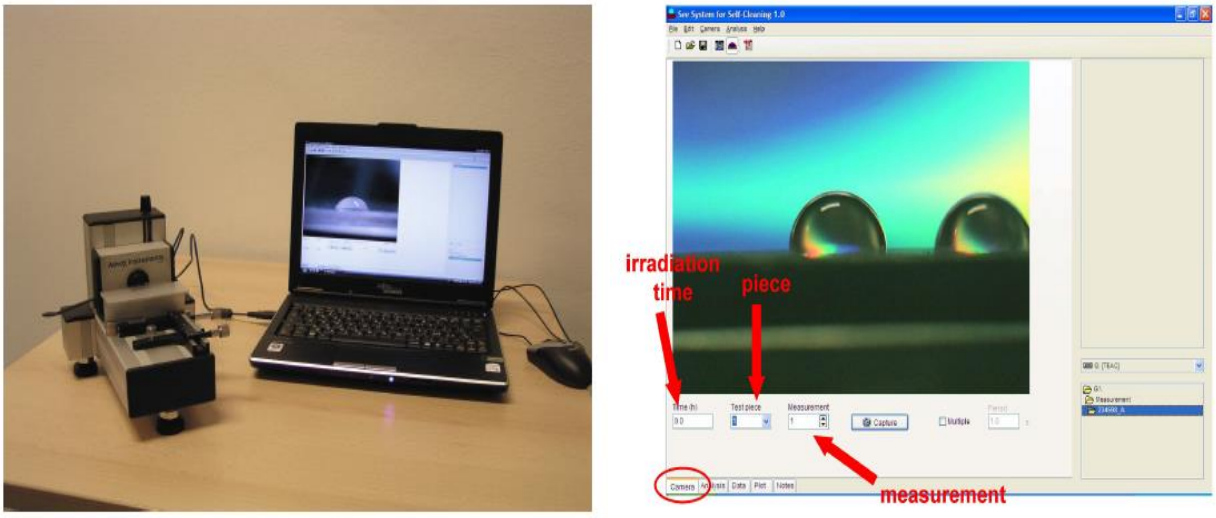


Figure 13. Advex instrument setup for contact angle measurement

The force involved when the water vapor interacts with the solid or fabric surface is given by Young-dupree equation:

$$\gamma_L \cos\theta = \gamma_s + \gamma_{SL} \quad (24)$$

where γ represents the interfacial tension that exists between the various combinations of solid, liquid, and vapor; the subscripts *S*, *L*, and *V* standing for solid, liquid, and vapor, and θ is the equilibrium contact angle.

The molecules on the surface of a liquid experience an imbalance of forces that contributes to the presence of free energy at the surface of the liquid. The excess energy is called 'surface free energy', for a liquid to wet a solid completely, or for the solid to be immersed in a liquid, the solid surfaces must have sufficient surface energy to overcome the free surface energy of the liquid. The surface free energy can be quantified as a measurement of energy per area. It is usually termed 'surface tension' and is quantified as force per length, with units' mN/m or dynes/cm

Table 2. Experimental plan and contact angle measurements for alkaline treatment of polyester film after acid treatment

Results of contact angle for polyester sheet (80% sulphuric acid)			Results of contact angle for polyester sheet (75 % sulphuric acid)		
Sample No.	Time of NaOH treatment [min]	Mean Contact angle [degree]	Sample No.	Time of NaOH treatment [min]	Mean Contact angle [degree]
Untreated	0	88.91 ± 2	Untreated	0	88.91 ± 2
S11	0.5	81.29 ± 2	S21	0.5	80.32 ± 2
S12	1	67.59 ± 2	S22	1	67.91 ± 2
S13	2	59.86 ± 2	S23	2	63.17 ± 2
S14	4	50.44 ± 2	S24	4	57.23 ± 2
S15	6	45.50 ± 2	S25	6	65.51± 2
S16	8	50.70 ± 2	S26	8	67.55 ± 2
S17	10	69.75 ± 2	S27	10	75.59 ± 2
S18	12	79.96 ± 2	S28	12	80.61 ± 2
S19	14	83.09 ± 2	S29	14	84.80 ± 2
S20	16	84.59 ± 2	S30	16	84.79 ± 2

4.6.2 Evaluation of surface free energy

The surface free energy of the modified polyester film is evaluated by using three liquids (distilled water, ethylene glycol, and diiodomethane) of known surface tension [87]. The liquids are supplied by Aldrich and are used without further purification. Surface tension components of liquids are reported in Table 3. Surface free energy (SFE) and critical surface tension is calculated by using the models proposed by Owens-Wendt, Li-Neumann and Zisman [88]. These methods allow to calculate the surface free energy using at least two liquids. The results obtained by one, two and three methods are combined according to the requirement of each method.

Table 3. Solvent surface tension components at 20 ˚C (mJ m^{-2})

Liquid	γ_d	γ_p	γ_t
Water	22.1	50.7	72.8
Ethylene Glycol	30.1	17.6	47.7
Diiodomethane	44.1	6.7	60.8

4.6.3 Evaluation of surface (Scanning Electron Microscope)

The surface changes after the treatment of acid and sodium hydroxide are observed by Scanning Electron Microscope (SEM) at high resolution. SEM is less surface sensitive as compared to other techniques and it is a well-established tool to observe the surface topography of the treated samples.

4.6.4 T-Peel test of adhesion

T-peel tests of adhesion are carried out on both untreated and treated samples on SANS universal testing machine with load cell of 30 kN and peel speed of 10 mm/min as ASTM D 1876-01 on rectangular specimens. Polyurethane resin is applied in order to join the treated substrates. Polyurethane resin is selected in order to test the change in surface free energy of the polyester substrate. The isocyanate present in the resin can react with the carboxylate ions generated after

the sodium hydroxide treatment on the polyester film surface. A static load is applied on the ends of the resin bonded substrates for a week at room temperature. The T-peel strength is determined on average of three samples.

4.6.5 Determination of specific surface area

The surface area is quantified by using the method developed by Brunauer, Emmett and Teller (BET method) which is an extension of Langmuir theory of monolayer adsorption to multilayer adsorption. The BET analysis is performed on Autosorb IQ, Quantachrome instrument, USA. The specific surface area is determined by N_2 absorption desorption isotherm at 77.35 K with relative pressure range P/P_o from 0.02 to 1, where P_o is the saturated pressure of nitrogen gas at 77.35 K(1 Atm). The samples are pre-treated in an oven at 45 ˚C for at least 5 hours and outgassed overnight at 150 ˚C.

4.6.6 Thermal properties

Thermal properties of the polyester film samples under investigation are evaluated in order to determine the thermal changes in the treated samples with heat flow. For the measurements a DSC 220 high sensitivity Differential Scanning Calorimeter is used with temperature rise of 10 ˚C/min under nitrogen flow and temperature is raised from room temperature to 400 ˚C.

CHAPTER 5
RESULTS AND DISCUSSION

5.1 Polyester fabric sodium hydroxide and urea Treatment

The results of percentage weight loss and wicking after pad-dry treatment of polyester fabric with caustic soda are shown in Table 4 and 5. The standard samples treated at 90 °C for 30 min with 50 g/l caustic soda has weight loss of 27.1 % and wicking height of 95 mm.

Table 4. 20 g/l NaOH treatment plan and results of percentage weight loss and wicking

No.	NaOH conc. [g/l]	Time of treatment [min]	Temperature [°C]	Percentage weight loss	Wicking [mm] Mean
1	20	2	130	0.96	32
2	20	4	130	1.09	35
3	20	6	130	1.78	35
4	20	8	130	2.56	35
5	20	2	150	1.14	40
6	20	4	150	1.18	40
7	20	6	150	1.25	40
8	20	8	150	2.32	40
9	20	2	170	1.12	40
10	20	4	170	1.45	40
11	20	6	170	1.58	40
12	20	8	170	2.35	40

Some experiments are conducted by the addition of 50 g/l urea (table 6) in the sodium hydroxide aqueous solution. Urea is a hygroscopic agent that can retain the moisture at hot drying conditions. The retention of moisture is very important in the completion of surface modification at hot dry conditions when the fabric is bone dry and only source of any humidity is the presence of humectant such as urea. The experiments are conducted with addition of urea in sodium hydroxide solution for surface hydrophilization of polyester and the time of treatment is varied as shown in table 6.

Table 5. 50 g/l NaOH treatment plan and results of percentage weight loss and wicking

Run order	NaOH conc. [g/l]	Time of treatment [min]	Temperature [°C]	Percentage weigh loss Mean	Wicking [mm] Mean
1	50	2	130	4.4	75
2	50	4	130	4.45	85
3	50	6	130	5.1	85
4	50	8	130	6.13	85
5	50	2	150	4.52	85
6	50	4	150	4.58	90
7	50	6	150	4.92	90
8	50	8	150	6.52	90
9	50	2	170	4.18	85
10	50	4	170	5.32	90
11	50	6	170	5.63	90
12	50	8	170	6.78	90

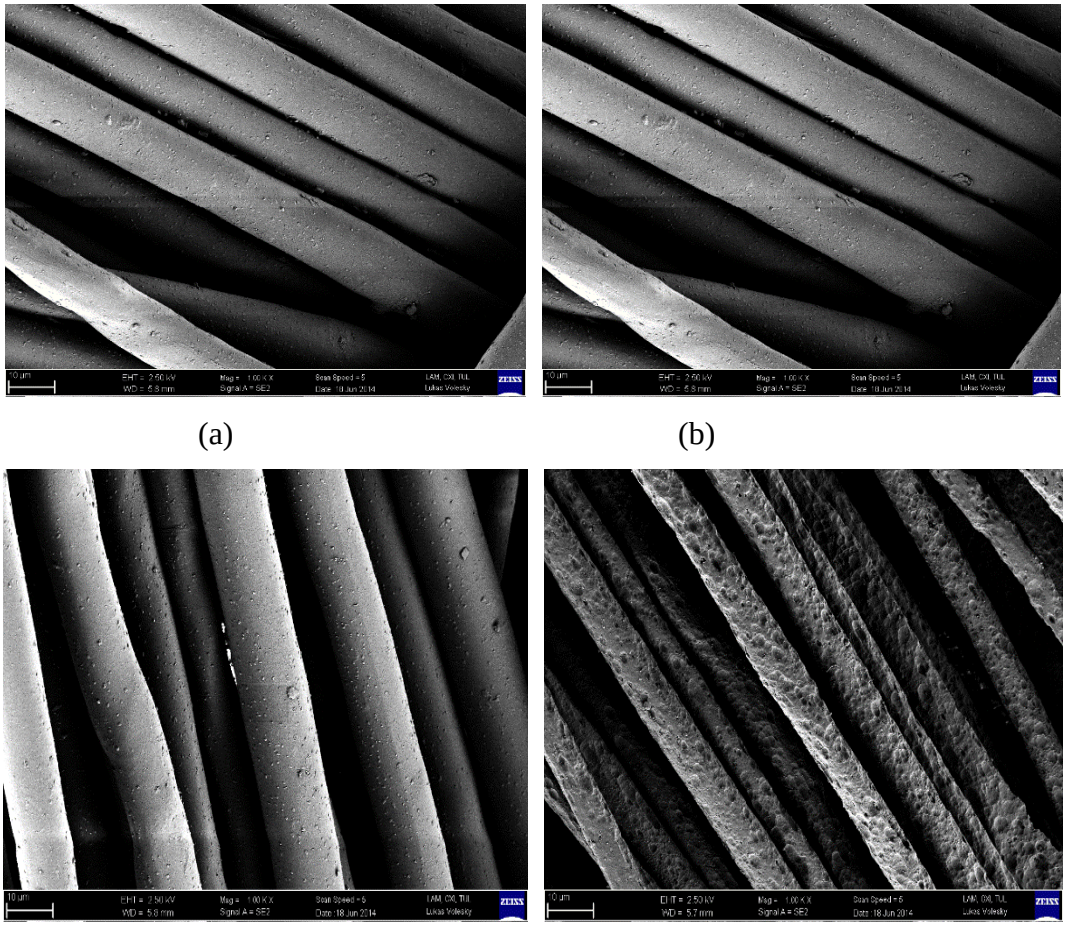
Table 6. 50 g/l NaOH and Urea treteatment and results of percentage weight loss and wicking

Experiment 2 (NaOH 50g/l, Urea 50 g/l) curing at 150 °C								
Treatment time	1 min	2 min	3 min	4 min	5 min	6 min	8 min	10 min
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
Wicking [mm] Mean	80	85	85	90	90	90	90	90
Mean Percentage Weight loss Mean	4.23	4.75	5.1	5.25	5.58	5.82	5.9	5.92

5.1.1 Alkaline hydrolysis

The figure 13 illustrates the surface morphology of the untreated and alkali treated polyester fabric samples. The SEM micrograph of untreated polyester fabric has almost the smooth surface. In the figure 13 (b) there is small pitting on the surface of the polyester fabric after the treatment with 20 g/l NaOH. In figure 13 (c) the pitting is more evident when saponification of polyester fabric is done with NaOH (50 g/l). The figure 13 (d) is the clear evidence of the alkaline hydrolysis of the polyester fabric after standard treatment for 30 min with caustic soda. The polyester fabric losses more weight as the yarns are thinned when treated at 90 °C with caustic soda as compared to the

only small surface pitting when treated with caustic soda by padding method. This is in agreement with the study carried out by F. Mousazadegan and his co-researchers [34]. The thinning of yarns is clearly avoided when the polyester fabric is treated by padding method.



(a) (b)

(c) (d)

Figure 14. (a) Untreated Polyester fabric, (b) Polyester fabric Pad-dry with NaOH (20 g/l) at 150 °C, (c) Polyester fabric Pad-dry with NaOH (50 g/l) at 150 °C, (d) Polyester fabric treated with NaOH (50 g/l) at 90 °C for 30 min

XPS is an extremely surface sensitive method allowing us to identify and quantify the chemical elements in the surface region of a solid and give information on the binding states of these elements, their oxidation numbers or functionalities. Figure 14 is the XPS micrograph of untreated polyester fabric. The spectra obtained by XPS measurement is the result of number of photoelectron incident on the specimen surface that are recorded as the function of binding energy with the groups present on the surface. There is change in the surface functionality and surface groups when polyester fabric is alkali treated. The percentage of C-O groups in the surface

increased from 10.66 % to 40 % in the alkali treated polyester, which is the clear evidence of the surface hydrolysis of polyester fabric after alkali treatment. In Figure 15 the XPS spectra shows some traces of nitrogen and OH-C=O as well that may be the attraction of water due to the presence of urea in the surface of polyester fabric.

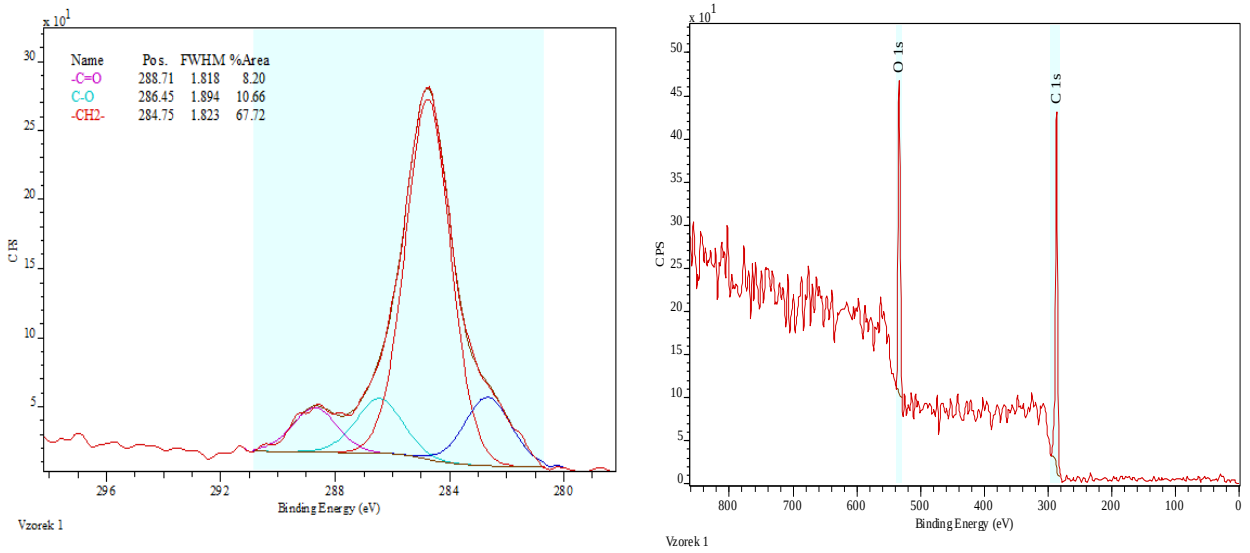


Figure 15. XPS micrograph of 100 % polyester

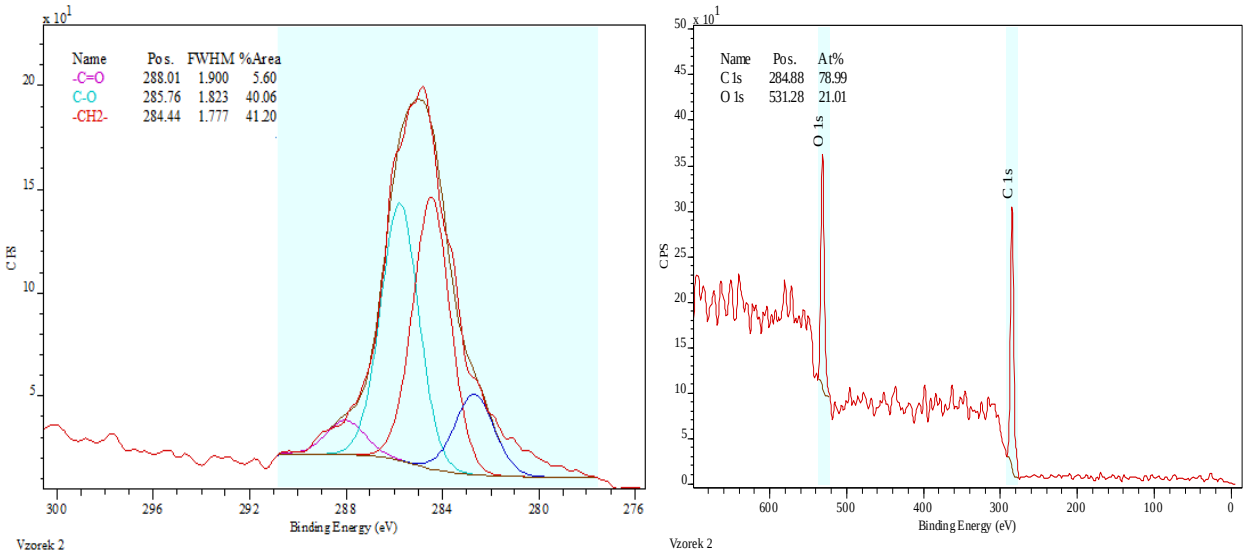


Figure 16. XPS micrograph of polyester fabric treated with 50 g/l NaOH at 150 °C for 4 min

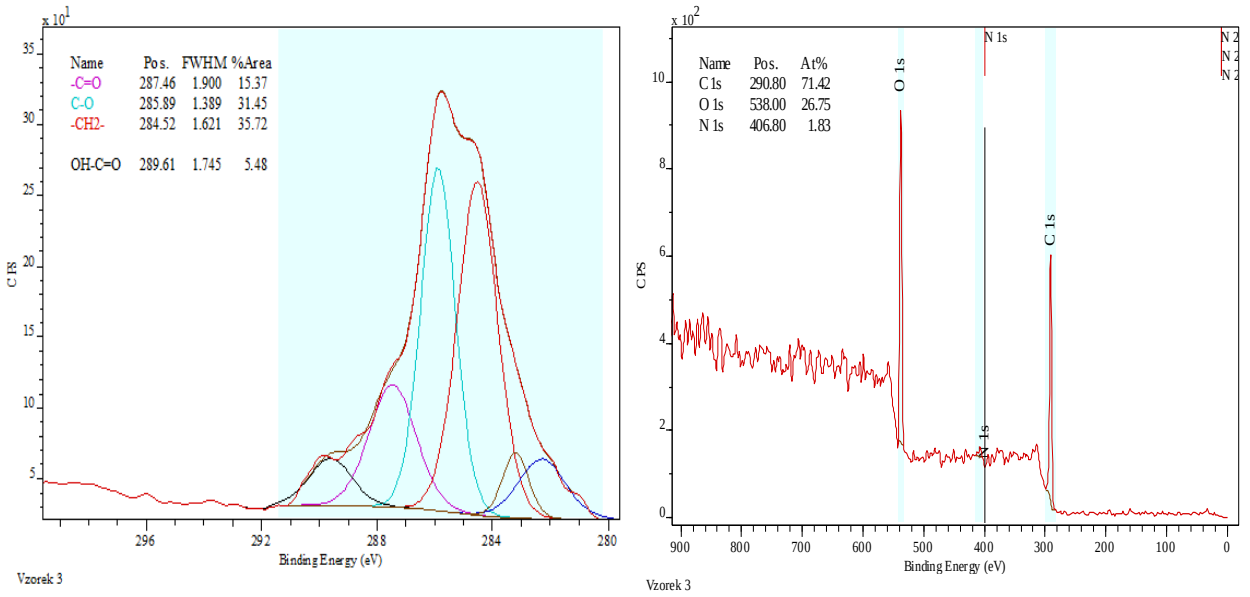


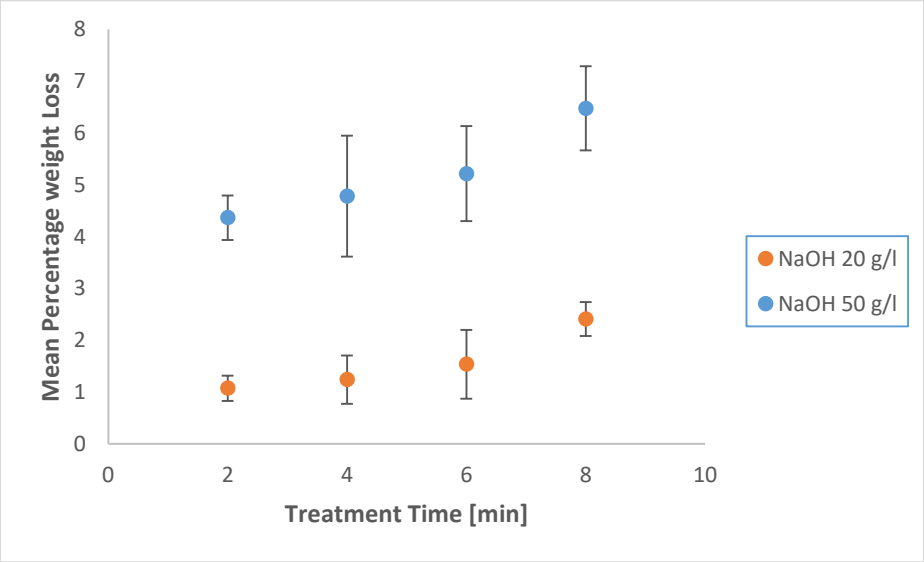
Figure 17. XPS micrograph of polyester fabric treated with 50 g/l NaOH and 50 g/l urea at 150 °C for 4 min

In addition to the qualitative determination of the surface composition of a understudy sample, the XPS method allows us also to quantify: the elemental composition and chemical environment of the species [89]. The effect of surface modification by sodium hydroxide is explained by the change in the surface composition of the treated samples. The C-O groups have increased in the surface of the NaOH modified polyester fabric that is the clear indication that the surface of PET fabric is successfully modified by the hot dry treatment under low liquor ratio by padding technology. Figure 16 has indicated the presence of –OH groups attached to the newly generated carboxyl groups is the indication towards the entrapment of urea as humectant on the surface of the polyester fabric that can contribute to the hydrophilization of polyester fabric.

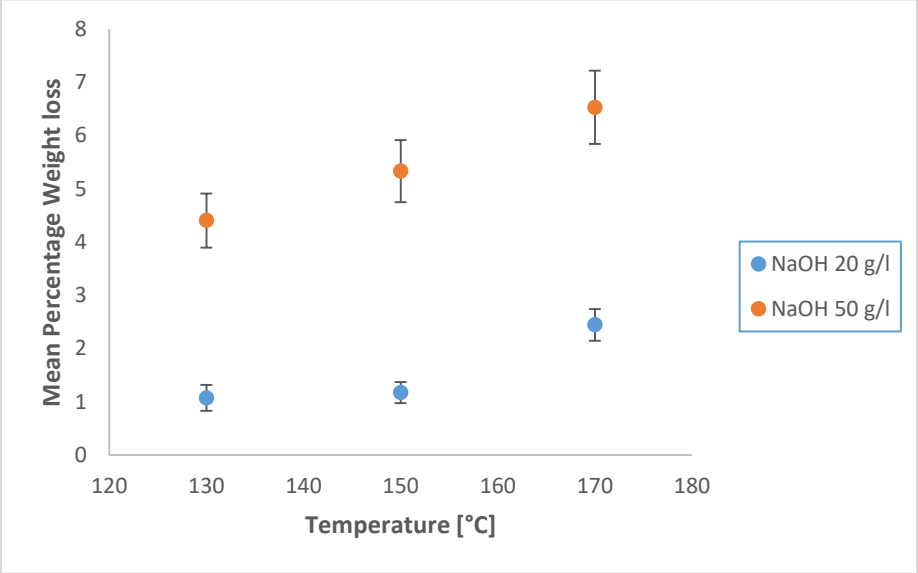
5.1.2 Loss in weight

The results percentage weight loss *(%WL)* of 100 % polyester fabric treated with NaOH (50 g/l) are shown in figure 17. The results of the study show that the weight loss has registered an increasing trend as the treatment time and temperature increases. When the fabric is treated without the addition of urea the weight loss is slightly more as it is reached to 6.78 % at the treatment time of 8 min. The weight loss is higher when polyester fabric is treated with standard caustic treatment at boil with increase in time of treatment. A high weight loss (27.1 %) was observed on treatment of polyester fabric with 50 g/l NaOH at 90 °C for 30 min. The Pad-dry samples show very little

weight loss when compared with the standard technique of polyester treatment with sodium hydroxide. The fabric weight loss also increases with the concentration of caustic soda increases from 20 g/l to 50 g/l.



(a)



(b)

Figure 18. (a)Effect of treatment time on Percentage Weight loss after NaOH treatment, (b) Effect of temperature on Percentage Weight loss after NaOH treatment.

The addition of urea in the caustic solution has the same effect on the weight loss of fabric as the polyester fabric is treated with the alkali solution only by pad dry method as depicted in figure 18.

The urea has in cooperated some in the interstices of the polyester fabric as shown by the XPS analysis of the urea treated fabric sample. The weight loss with urea addition in alkali solution fall with in the similar values when compared with the alkali treated pad dry polyester fabric samples. The weight loss is significantly low when compared with standard treatment. It is noticed that the weight loss has progressive reduction with decrease in temperature. It is in conformity with the proposed work of heat setting [90].

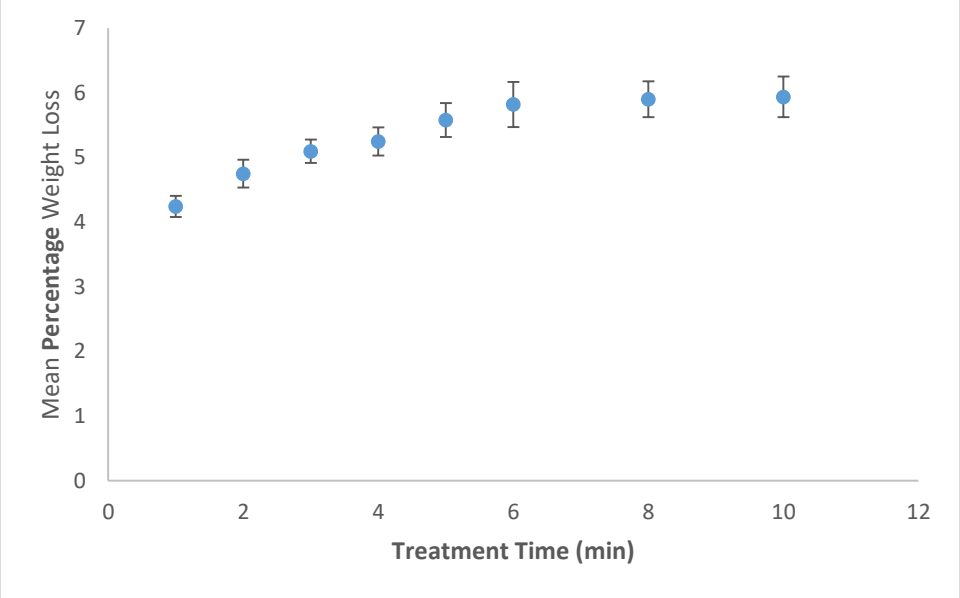


Figure 19. Effect of treatment time on percentage weight loss of polyester fabric after NaOH and urea treatment

5.1.3 Wicking

The wicking behavior of polyester fabric treated with caustic soda and urea is shown in the figure 19 and 20. The wicking of untreated sample is only 15 mm. In figure 19 the wicking is related with the time of treatment of the fabric. It is quiet noticeable that the wicking height shows increasing trend as the wicking height shows increasing trend when concentration of sodium hydroxide is increased from 20 g/l to 50 g/l with the increasing treatment time. The maximum wicking height for both the samples whether caustic treated with padding method and by standard treatment is 90 mm and 95 mm respectively. The alkali treatment of the polyester fabric in both conditions causes partial hydrolysis of the polyester yarns which causes the capillary formation with in the bundle of fibers that may be the reason of better wickability than the untreated polyester fabric. It was observed that the water was absorbed progressively in the small amounts on the fabric surface

suggesting that there is some change in the morphology of the fibers due to the formation of pits on the surface of yarns.

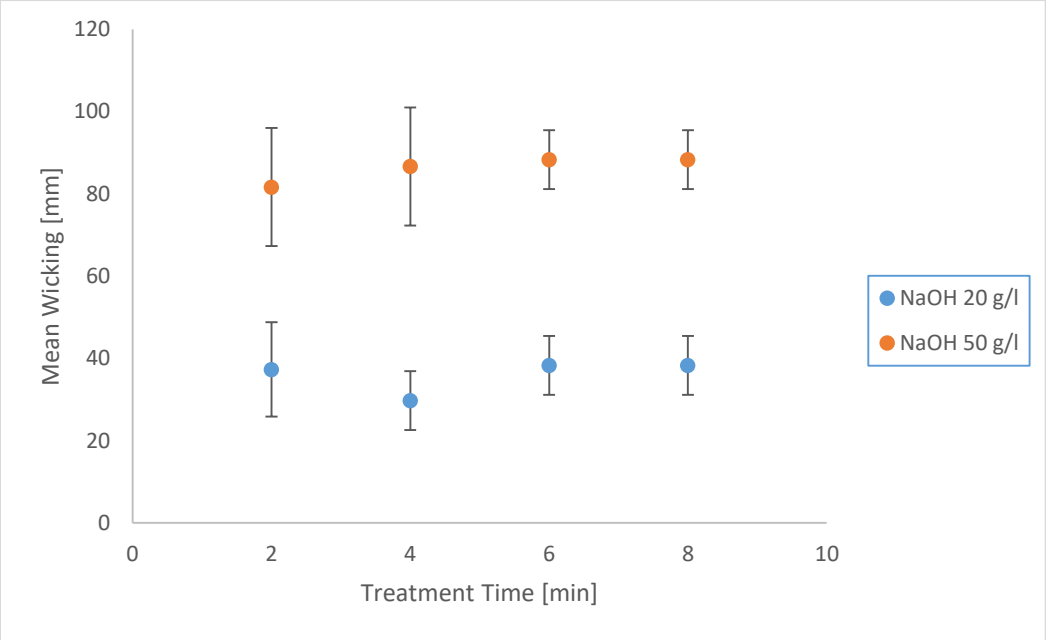


Figure 20. Effect of treatment time on wicking height of polyester fabric

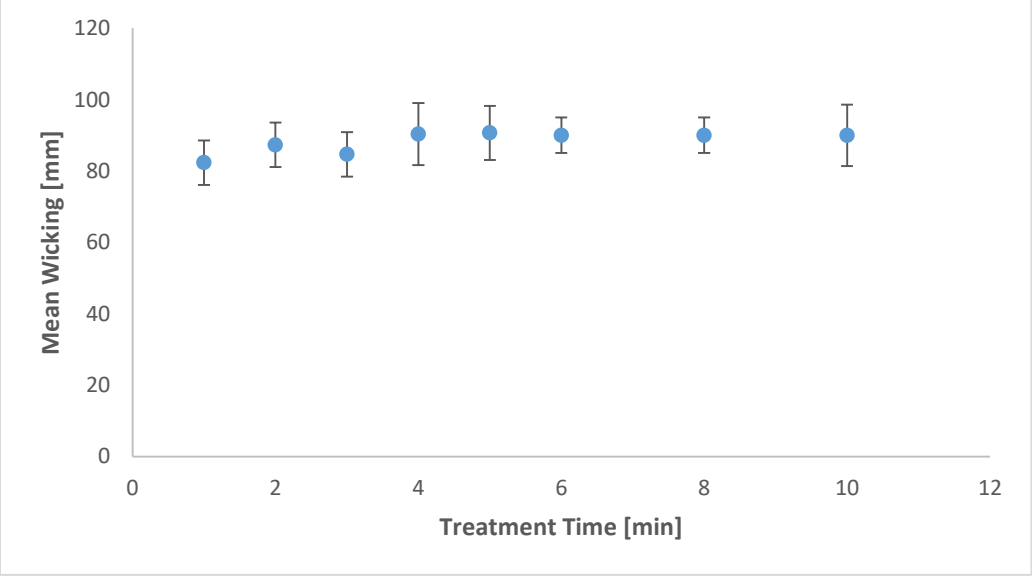


Figure 21. Effect of treatment time on wicking of polyester fabric after NaOH and urea treatment

The flow of liquid moisture through textiles is caused by fiber-liquid molecular attraction at the surface of the fibrous materials, which is mainly determined by the surface tension and the effective capillary pore distribution and pathways. Liquid transfer through a porous structure

involves two sequential processes – wetting and wicking. Wetting is the initial process involved in fluid spreading. Wicking starts as soon as the area in contact with water becomes saturated. So the hydrolysis by sodium hydroxide causes the water to attract to the fabric surface and then this water passes through the pores of the polyester fabric through wicking. The results of wicking height related to the time of treatment by pad-dry method treated with 50 g/l NaOH and urea are shown in Fig 20. The wicking obtained has values from 70 mm to 90 mm at all selected time of treatments. The pad-dry method the longer time of treatments seems to have no significant effect on the fabric wicking and absorbency properties. The hygroscopic nature of the urea has not contributed to the water retention ability of the polyester fabric as the wicking heights fall in the same region i.e. 90 mm when compared with alkali pad –dry and standard treated polyester fabric samples.

5.2 Polyester fabric glycerin treatment in presence of sodium hydroxide

The experimental plan and results of percentage weight loss and wicking after pad-dry treatment of polyester fabric are shown in Table 7 and 8. The glycerin treatment is carried out with 20g/l and 50 g/l NaOH concentration at temperature of 180 °C and dried for 2 min.

Table 7. Experimental plan for Glycerin treatment in presence of 20 g/l NaOH

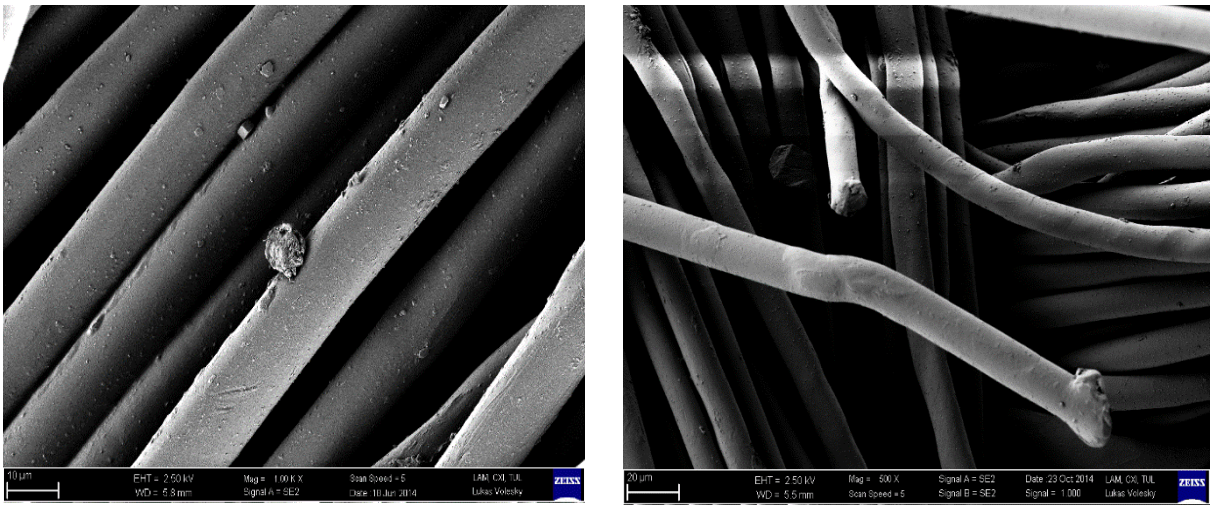
Experiment (NaOH 20g/l) drying at 180 °C for 2 min								
Glycerin conc. [g/l]	10	20	50	80	100	120	150	200
	Sample 1	Sample 2	Sample 3	sample 4	Sample 5	Sample 6	Sample 7	Sample 8
Wicking [mm] Mean	55	65	85	95	95	95	80	65
Percentage Weight loss Mean	3.6	3.7	3.6	3.8	3.9	3.7	3.8	3.7

Table 8. Experimental plan for Glycerin treatment in presence of 50 g/l NaOH

Experiment (NaOH 50g/l) drying at 180 °C for 2 min								
Glycerin conc. [g/l]	10	20	50	80	100	120	150	200
	Sample 1	Sample 2	Sample 3	sample 4	Sample 5	Sample 6	Sample 7	Sample 8
Wicking [mm] Mean	70	70	90	95	95	100	100	95
Percentage Weight loss Mean	7.9	8	8.0	7.9	8.1	8.2	8.4	8.4

5.2.1 Weight loss

Figure 21 shows the effect of changing glycerin concentration on the weight loss of polyester fabric in alkaline solution of 20 g/l NaOH treated for 2 minutes at temperature of 180 °C. All the samples with different glycerin concentration are treated at same alkaline, time and temperature conditions. Increasing the glycerin concentration the percentage weight loss remains in the region of 3 to 4 %. Figure 22 shows the result of glycerin treatment in 50 g/l NaOH alkaline conditions and treated for 2 minutes at temperature of 180 °C. With the increase in concentration of alkali the weight loss is increased in the range of 7 to 8 %. The similar kind of weight loss is observed with pad dry treatment of polyester fabric with 50 g/l NaOH treatment. The weight loss is only associated with the presence of alkali and glycerin does not contribute to the weight loss of polyester fabric. This may be due to the fact that sodium hydroxide causes the nucleophilic substitution reaction the surface of the polyester that contributes to the peeling of the surface and ultimately leading to the weight loss while glycerin is an organic component that only adhere to the surface of the polyester fabric and forming a layer on the surface as indicated by the SEM micrograph of glycerin treated polyester fabric.



(a) (b)

Figure 22. (a) Untreated polyester fabric (b) Glycerin treated polyester fabric with 100 g/l glycerin, 50 g/l NaOH, temperature 180 °C and time 2 min.

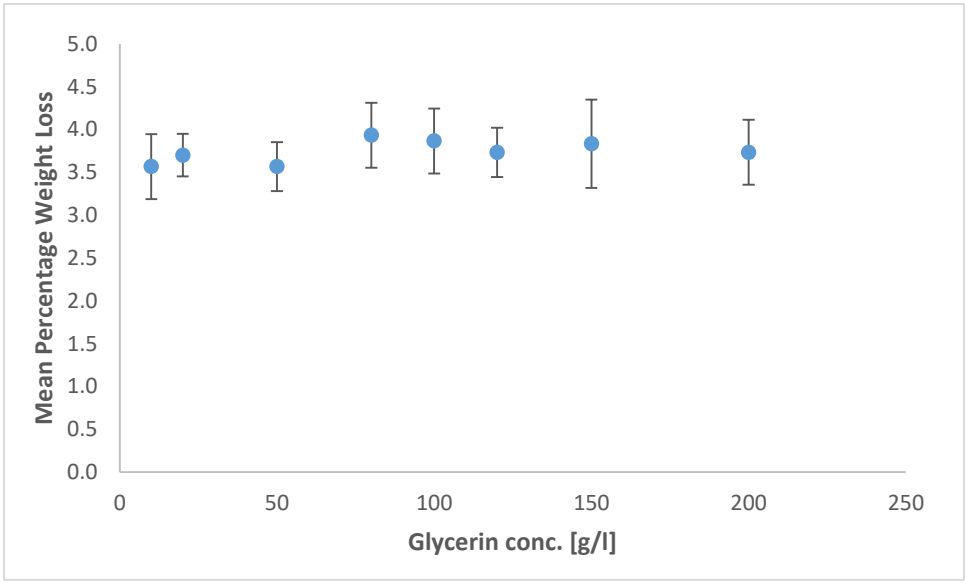


Figure 23. Effect of Glycerin concentration on percentage weight loss of polyester fabric in presence of 20 g/l NaOH

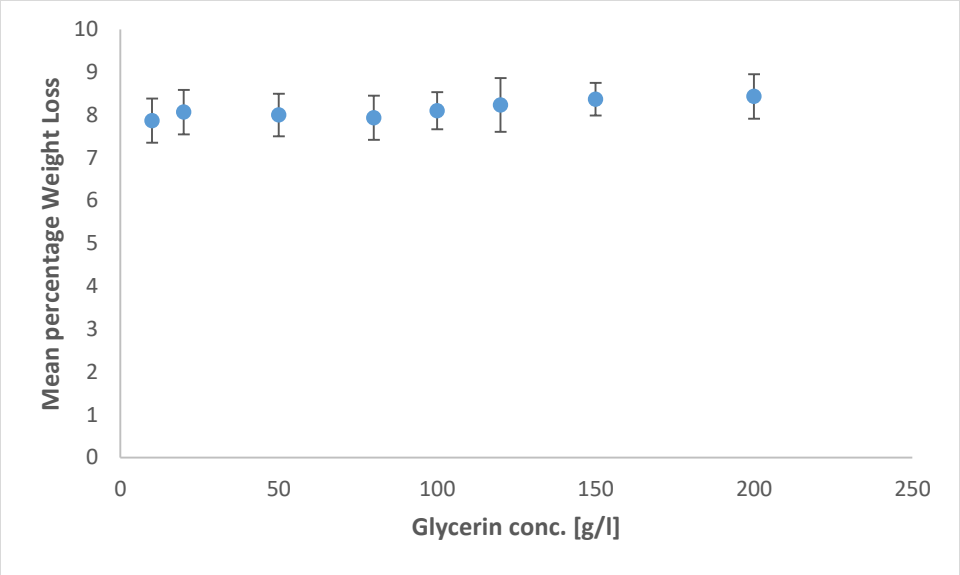


Figure 24. Effect of Glycerin concentration on percentage weight loss of polyester fabric in presence of 50 g/l NaOH

5.2.2 Vertical Wicking

The results of wicking with changing concentration of glycerin in solution of 20 g/l NaOH and 50 g/l NaOH are shown in figure 24 and 25. As the concentration of glycerin increases the wicking height first increases and then at higher concentration shows decreasing trend in low concentration alkali solution. In 50 g/l solution of alkali the wicking height first increases and then it becomes almost constant with changing amount of glycerin. This treatment depicts the maximum wicking height of 100 [mm] at glycerin concentration of 120 g/l in solution of 50 g/l. The dilute solution of 20 g/l NaOH also give the wicking height of 95 [mm] at the same glycerin concentration of 150 g/l as given by the strong alkali solution. The glycerin provides a hydrophilic layer on the surface of the polyester fabric that contributes to the greater wicking heights as compared to the untreated one that has very low value of 18 [mm].

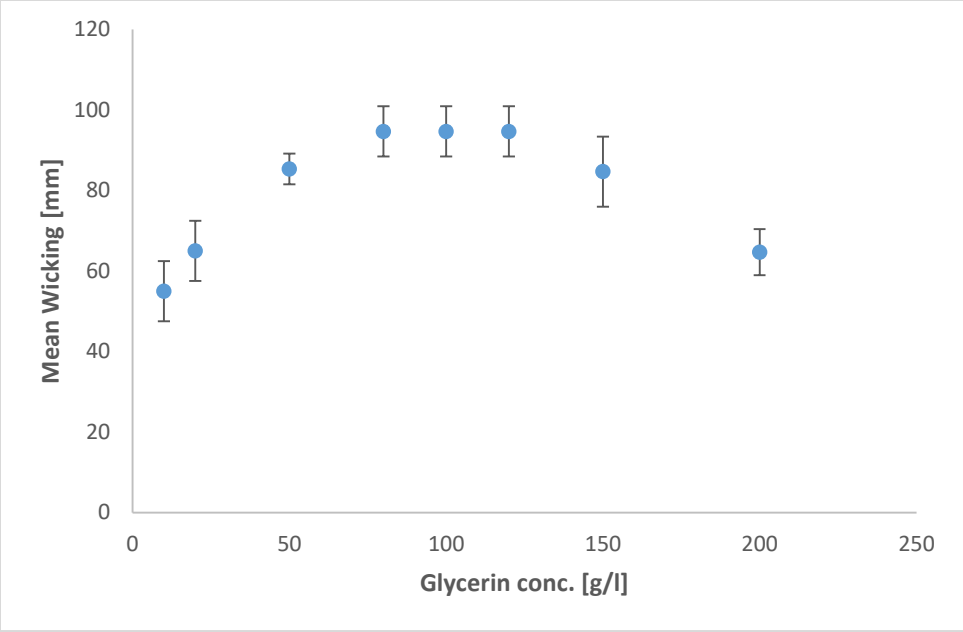


Figure 25. Effect of Glycerin concentration on wickability of polyester fabric in presence of 20 g/l NaOH

The hygroscopic agent like glycerin attaches to the surface of the warp and weft of the polyester fabric in the presence of sodium hydroxide that is also the source of hydrophilization of polyester. This contributes to the wetting of the spaces of the yarns that produces the capillary pressure for water to rise in between the spaces or voids of the fabric. First the wetting of the hydrophobic fabric is required and then a good wicking in order to quickly spread the liquid with in the fabric for an even distribution and greater surface area in order to dry the liquid quickly for better comfort level.

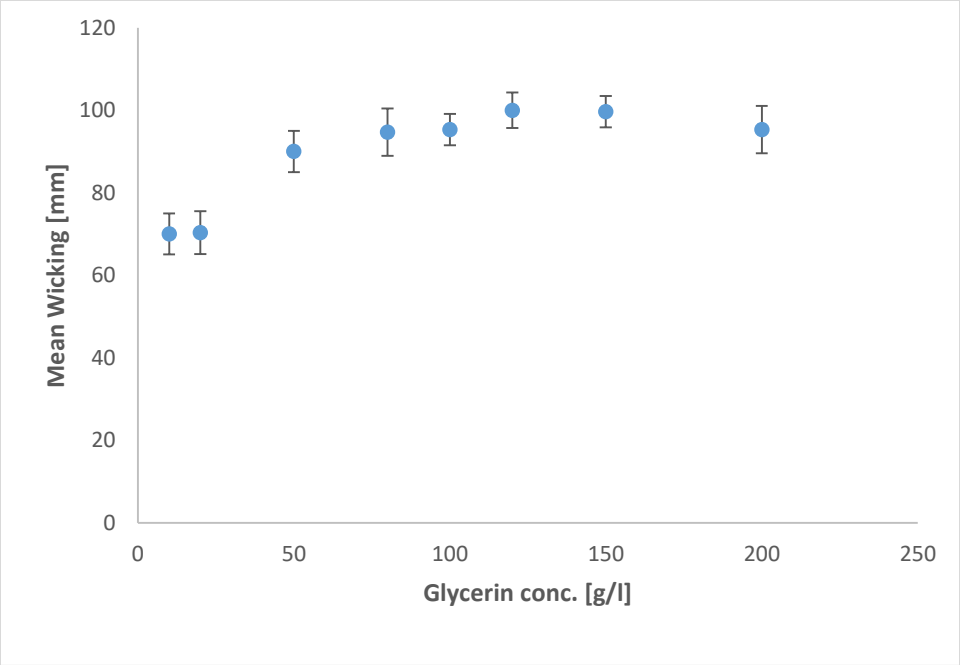


Figure 26. Effect of Glycerin concentration on wickability of polyester fabric in presence of 50 g/l NaOH

5.3 Optimization of Alkali treatment parameters

The alkali treatment parameters are estimated by using the Box–Behnken experimental design, thirty runs with appropriate combinations of NaOH concentration, Time and temperature of treatment were conducted. The results for percentage weight loss and vertical wicking are given in table 9. The alkali like sodium hydroxide causes the surface hydrophilization of polyester fabric leading to the potential hydrophilic groups on the surface of the polyester. The low concentration alkali treatment by padding under controlled conditions causes the increase in the wicking and weight loss of the fabric. The weight loss by this padding method is far less than the general standard method at longer cycles of the alkali treatment. The experimental results in the table were fitted to a full quadratic second order model by applying multiple regression analysis using MINITAB software. The one repetition of the selected experiments is also include in the design in order to minimize the experimental errors that occurs during the performance of the experiment runs. The model equations representing percentage weight loss and wicking are expressed in terms of SHC, TIME and TEMP for actual values of variables as given in equation 25 and 26.

$$\boldsymbol{Percentage\ weight\ loss} = 1.35 - 0.0224.SHC - 0.706.TIME + 0.002.TEMP + 0.001.SHC^2 - 0.038.TIME^2 - 0.001.\ TEMP^2 + 0.003.SHC.TIME + 0.001.SHC.TEMP + 0.006.TIME.TEMP \quad (25)$$

$$\boldsymbol{Vertical\ Wicking} = -690 + 0.86.SHC + 26.21.TIME + 8.47.TEMP - 0.069.SHC^2 - 0.028.\ TEMP^2 + 0.034.SHC.TEMP - 0.172.TIME.TEMP \quad (26)$$

Table 9. Box-Behnken design showing obtained properties of hydrophilized polyeser fabric

Run	Sodium hydroxide concentration [g/l]	Time [min.]	Temperature [˚C]	Percentage weight loss	Vertical Wicking [mm]
1	20	6	150	1.25	40
2	20	4	130	1.09	35
3	35	2	130	2.16	45
4	35	6	170	3.43	75
5	20	2	150	1.18	40
6	50	6	150	4.92	90
7	35	2	170	2.24	75
8	35	2	170	2.3	75
9	20	6	150	1.25	40
10	20	4	170	1.48	40
11	35	4	150	2.76	80
12	35	2	130	2.52	45
13	50	4	170	5.38	90
14	20	4	130	1.1	35
15	50	6	150	5.06	90
16	35	6	130	2.67	75
17	50	4	130	4.45	43
18	35	4	150	2.94	80
19	20	2	150	1.14	40
20	35	4	150	3.02	80
21	35	6	170	3.38	80
22	50	2	150	4.52	85
23	35	4	150	2.97	80
24	50	2	150	4.47	85
25	35	4	150	3.04	80
26	35	4	150	2.9	75
27	35	6	130	2.36	75
28	20	4	170	1.45	40
29	50	4	170	5.32	90
30	50	4	130	4.4	45

For the estimation of significance of the model, the analysis of variance and the F-test were carried out. The corresponding variables would be more significant when the absolute F-value becomes greater and the p-value (significance probability value) becomes smaller. Using 95 % confidence level, a model is considered highly significant if the p-value is less than 0.05. From the p-value presented in table 10 and 11, it can be concluded that the linear, quadratic and interaction contributions for both percentage weight loss and vertical wicking are highly significant. The coefficient of determination is found to be 96.82 % for percentage weight loss model and 87.19 % for vertical wicking model, which means that the model could explain 96.82 % and 87.19 % of the total variations in the system.

Table 10. Estimation of significance of model for percentage weight loss

Source	Degree of Freedom [DF]	Sum of Squares [SS]	Mean Square [MS]	F-value	p-value
Regression	9	53.87	5.98	170.7	0.001
Linear	3	53.06	17.69	942.67	0.003
Quadratic	3	0.485	0.162	4.62	0.013
Interaction	3	0.787	0.26	7.49	0.002
Residual error	20	0.701	0.035		
Lack of fit	3	0.105	0.04	1.00	0.418
Pure error	17	0.59	0.035		
Total error	29	54.57			

Table 11. Estimation of significance of model for vertical wicking

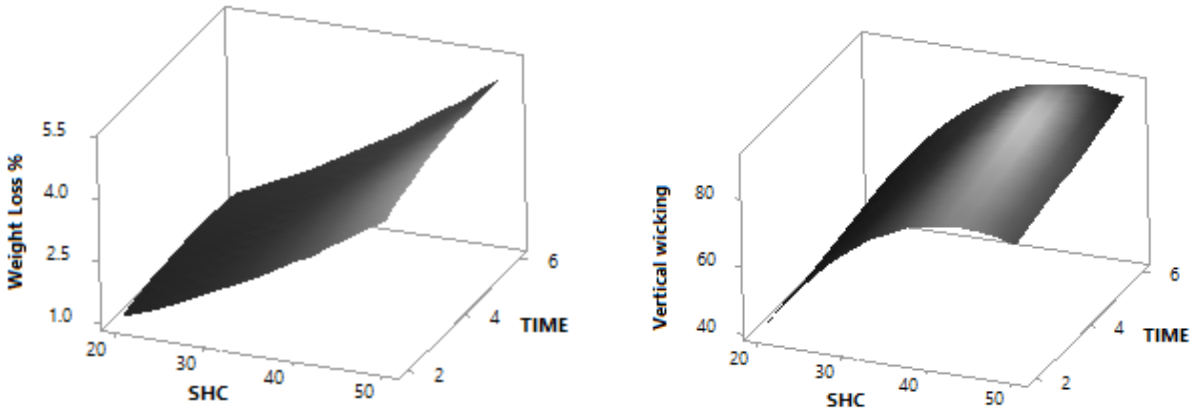
Source	Degree of Freedom [DF]	Sum of Squares [SS]	Mean Square [MS]	F-value	p-value
Regression	9	11849.9	1316.66	41.54	0.001
Linear	3	8023.6	2674.54	84.38	0.001
Quadratic	3	2595.2	865.05	27.29	0.001
Interaction	3	1231.1	410.37	12.95	0.001
Residual error	20	634.0	31.70		
Lack of fit	3	598.6	199.54	96.01	0.001
Pure error	17	35.3	2.08		
Total error	29	12483.9			

The statistical significance of the each factor as a function of p-value (at 95 % confidence) based on the analysis of the variance of data is shown in table 12.

Table 12. Analysis of variance for effect of input variables on response variables

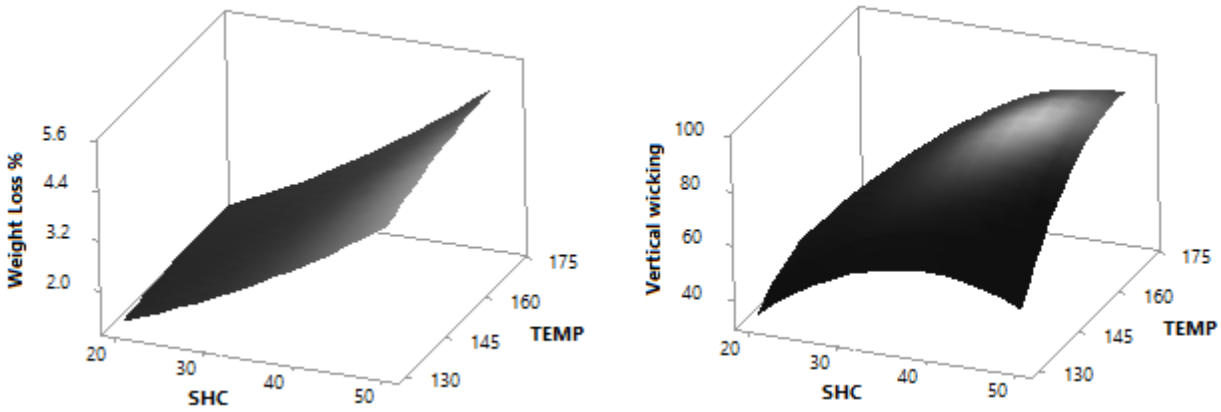
Terms	Percentage weight loss		Vertical wicking [mm]	
	Coeff.	*p-value*	*Coeff.*	*p-value*
SHC	1.786	0.000	19.25	0.000
TIME	0.182	0.001	4.69	0.003
TEMP	0.253	0.000	10.44	0.000
SHC^2	0.188	0.013	-15.65	0.000
$TIME^2$	-0.152	0.038	0.23	0.913
$TEMP^2$	-0.042	0.540	-11.27	0.000
SHC.TIME	0.101	0.142	1.25	0.537
SHC.TEMP	0.138	0.049	10.25	0.000
TIME.TEMP	0.262	0.001	-6.88	0.003

From the analysis of variance it is evident that the percentage weight loss and wicking are significantly affected by the surface hydrophilization parameters for polyester fabric by pad-dry method under the tension state. The three dimensional plots of response surface model are studied for the interaction effect of surface hydrophilization factors on percentage weight loss and wicking. The plots are shown from figure 26 to 28. The development of carboxyl groups after the alkali treatment of polyester fabric causes the hydrophilicity to increase and water to rise in the capillaries of the fabric in connection with water loving groups present on the surface of the polyester fabric. This behavior is attributed to the gradual reaction of sodium hydroxide with the polyester that leads to the surface pitting to occur by hydrophilization reaction. The three factors under study have a pronounced effect on the weight loss and vertical wicking of the polyester fabric. It is evident from the figure 26 (a) and (b) that the effect of sodium hydroxide concentration is more pronounced in the increase of the weight loss percent and vertical wicking than the time and temperature of the treatment of polyester fabric. As the temperature increases the more time the polyester fabric attains at the drying condition for the reaction of sodium hydroxide to execute properly, thus greater surface hydrophilization is achieved that leads to the increase in the suction height after the treatment. From the results it is clear that all these factors after interacting with each other cause strong influence on percentage weight loss and vertical wicking of the hydrolyzed polyester fabric.



(a) (b)

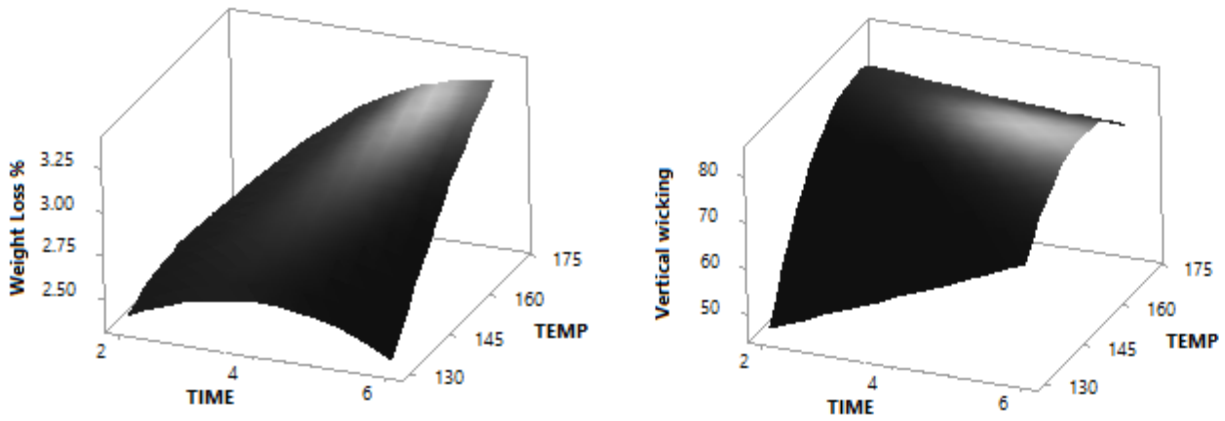
Figure 27. Effect of (a) SHC and TIME on percentage weight loss and (b) SHC and TIME on vertical wicking



(a) (b)

Figure 28. Effect of (a) SHC and TEMP on percentage weight loss and (b) SHC and TEMP on vertical wicking

The results has indicated that among the three concentrations of sodium hydroxide the 50 g/l gives the best results for the vertical wicking of the under study substrate.



(a) (b)

Figure 29. Effect of (a) TIME and TEMP on percentage weight loss and (b) TIME and TEMP on vertical wicking

With the help of response optimizer in MINITAB software, set of optimized parameters for both percentage weight loss and vertical wicking are calculated and given in Table 13.

Table 13. Optimum values of hydrophilization parameters

SHC (g/l)	TIME (min)	TEMP (˚C)	Percentage Weight Loss	Vertical Wicking [mm]
40.5	4	150	3.67	85.5

5.4 Stability of Surface hydrophilization of polyester fabric

The polyester fabric is treated at optimized conditions for wicking and then its vertical wicking is observed. This fabric is tested for the thermal stability of the surface hydrophilization at different temperatures. The idea is to evaluate the durability of the alkali treatment by pad-dry method by placing at different temperatures for a specified length of time. Polyester is chemically treated with alkali, there are more chances that the surface of the polyester is chemically modified, this chemically modified surface retains its hydrophilic groups even at elevated temperatures with only small change from the room temperature hydrophilicity. The physical surface modification techniques, like plasma and ozone treatments, for improved surface hydrophilicity of polyester tends to fade away as the temperature of service increases. There is need that the polyester fabric

treated with physical treatments must be after treated immediately in order to have a permanent effect or to have full advantage of the treatment.

The optimized polyester fabric samples are placed at five different temperatures (20, 60, 100 and 120) for longer periods of times (0.5, 1, 2, 3, 4, 5 and 6 days). The plasma and ozone treatment is also done in order to compare the thermal stability of alkali treatment with these physical treatments. The vertical wicking is observed and reported in table 14.

Table 14. The results of vertical wicking at different performance temperatures and holding time

No. of Days	Sodium hydroxide treatment				Plasma treatment				Ozone treatment			
	Vertical Wicking [mm]				Vertical Wicking [mm]				Vertical Wicking [mm]			
	20 ˚C	60 ˚C	100 ˚C	120 ˚C	20 ˚C	60 ˚C	100 ˚C	120 ˚C	20 ˚C	60 ˚C	100 ˚C	120 ˚C
0	90	90	90	90	60	60	60	60	45	45	45	45
0.5	90	90	87	87	55	40	30	28	40	37	27	25
1	90	90	87	87	52	36	28	25	38	35	25	21
2	90	90	87	85	50	33	25	20	36	35	23	18
3	90	90	87	85	47	30	23	20	33	30	20	18
4	90	90	87	85	45	28	23	18	33	28	20	18
5	90	90	87	85	45	28	20	18	30	23	18	18
6	90	90	87	85	44	26	20	18	30	23	18	18

Each sample is hold at specified temperature and then it is conditioned and tested for vertical wicking, for example, an alkali treated fabric sample at optimized parameters is placed at 20 ˚C in the oven for half day (12 hours) then it is removed from the oven, conditioned and tested for vertical wicking values. The zero days means the fabric sample is tested just after the treatment without placing at any holding temperature. The flow of liquid in fiber assemblies, such as yarn

and fabric, happens because of capillary forces. In the field of liquid sorption in a porous area, Washburn has expressed the following equation [38]:

$$h = a.t^{0.5} \tag{27}$$

Where *h* is the wicking height (m): *a* capillary liquid transport constant and *t*, wicking time (s). Laughlin showed the need of correction in the exponent term and many researchers suggested that the exponent should be lower than 0.5. Hence, Laughlin generalized the Washburn's equation into the following form:

$$h = a.t^{k} \tag{28}$$

Where *k* may have values lower than 0.5 for different types of fabrics. This capillary force depends on the radius of capillary channel and the contact angle between liquid and capillary channel as well as rheological properties of the liquid. This equation is used to calculate the suction height (Vertical Wicking) from the experimental values as shown in table 14. The following relation is established between the maximum suction heights and time constant *k*:

$$SH = SH_{max} - a\,.\sqrt[4]{1 - e^{(-kt)}} \tag{29}$$

Where *SH* is the Vertical Wicking, SH_{max} is the maximum vertical wicking that can be achieved in the experimental data, *k* is rate constant and *t* is holding time. The vertical wicking obtained from the equation (29) is plotted against the no. of days the fabric sample is placed at particular temperature. Figure 29 represents the change in the wicking of the polyester samples with increase in temperature and length of time in terms of days the plasma treated polyester fabric samples are placed at each temperature. It is evident from the obtained data is that the vertical wicking has decreasing trend as the working temperature is increased from 20 ˚C to 120 ˚C. The decrease in vertical wicking is not so high with increase in exposure time at low temperature but at high temperature there is significant decrease in vertical wicking even at half day of exposure time. It is apparent that the increase in wettability of the single fiber surfaces via surface oxidation through plasma treatment may have enhanced water wicking into the fibrous assembly. This method of hydrophilization of polyester is highly probable to the loss of hydrophilization as the time of exposure to atmosphere or temperature of exposure increases. The oxidized polymer surfaces tend to arrange themselves in such a way that the surface of polyester polymer is again have polymer

groups that are either not modified or least modified showing hydrophobic properties and ultimately leads to the decrease in vertical wicking of the plasma treated polyester fabric.

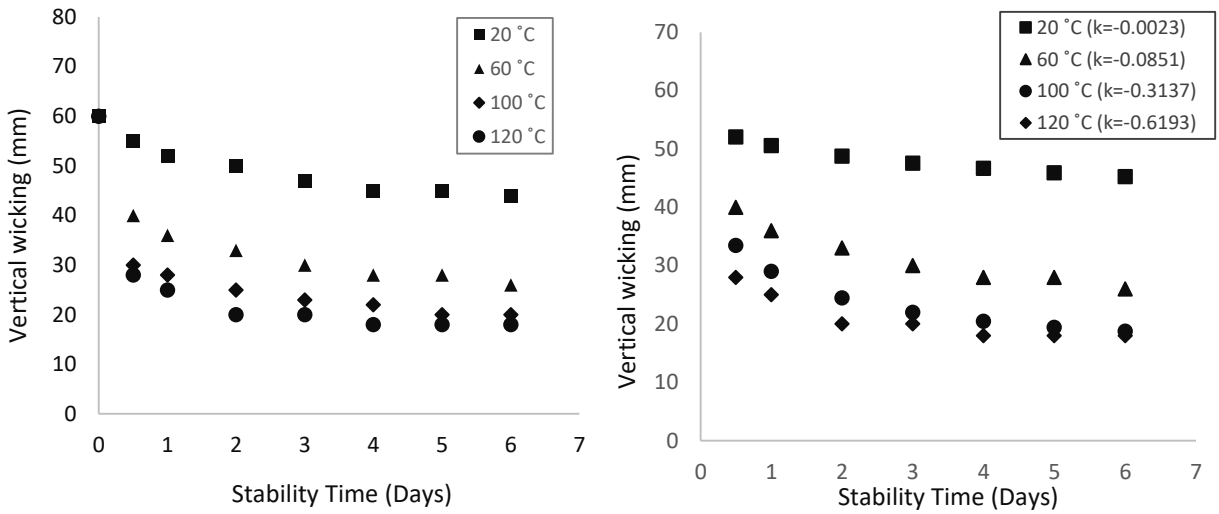


Figure 30. Effect of stability time on vertical wicking of polyester fabric after plasma treatment at various temperatures.

The results of wicking of ozone treated polyester samples after placing at different temperatures are depicted in the figure 30. It is evident from the plot that the vertical wicking after ozone treatment is far less than the alkali treatment by pad-dry method. The water absorption capacity of the polyester fabric is increased a little after the ozone treatment. When the fabric is placed at lower temperature it generally hold the oxidized modification and there is some hydrophilicity in the polyester fabric. The higher temperatures tend to lower the wicking rate and thus in turn the water holding capacity of the polyester fabric is certainly lowered. Ozone-gas treatment of the polyester fabrics brought about not only changes in the surface wettability but also changes in the internal fine structure in the crystalline and amorphous regions of the polyester fiber. Ozone gas treatment is highly unstable at temperature 120 ˚C. The oxidized surface changes in the polyester fabric tend to disappear and again the water attraction of the polyester fabric is minimized which leads to the less wicking rate of the understudy polyester fabric.

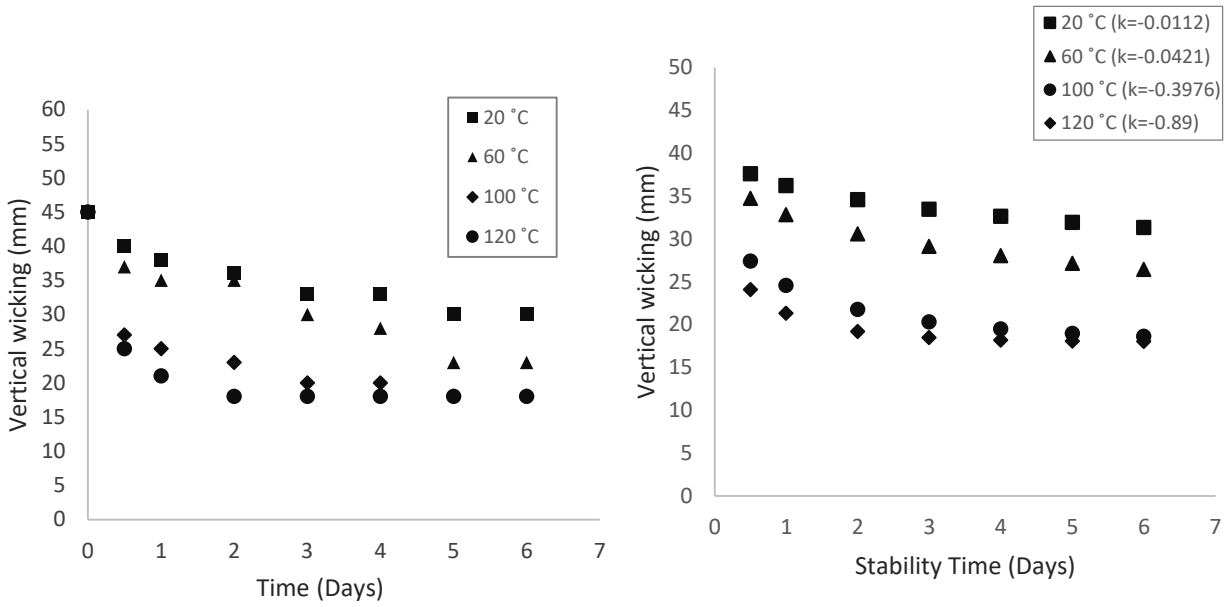


Figure 31. Effect of stability time on vertical wicking of polyester fabric after ozone treatment at various temperatures.

The vertical wicking of the polyester fabric after pad-dry treatment at optimized conditions with stability at different temperatures are shown in figure 31. The surface modification produced by this method tends to stabilize itself at different elevated temperatures and longer holding time. Liquid transfer mechanisms include water diffusion and capillary wicking, which are determined mainly by effective capillary pore distribution, pathways and surface tension, whereas the drying rate of a material is related to the macromolecular structure of the fiber. As capillary forces are caused by wetting, wicking is a result of spontaneous wetting in a capillary system. Wicking takes place only in wet fabrics or when fabrics come into contact with water, and the contact angle determines their wicking behavior. A lower contact angle results in higher wicking rates. The wicking behavior of fabrics is mainly determined by the effective capillary pore distribution and pathways as well as surface tension. The alkali modification has produced oxidized groups that tend to be permanent and are not affected by the high temperature and longer stability times.

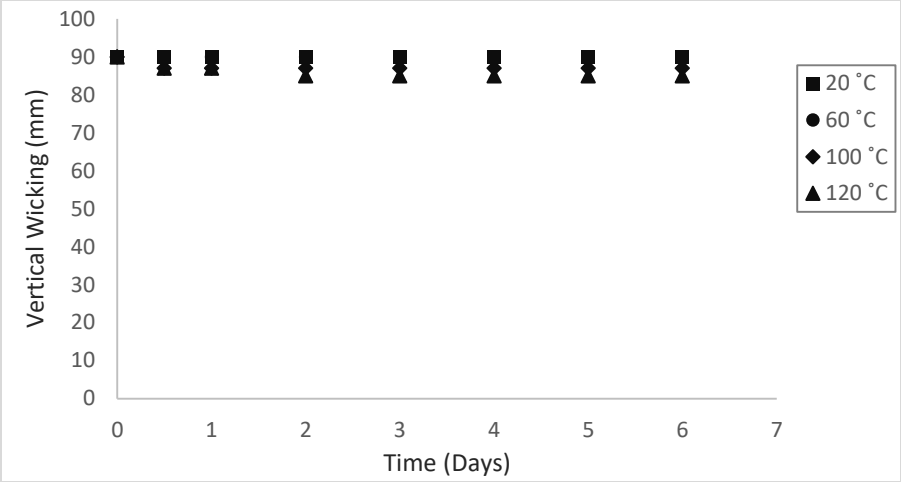


Figure 32. Effect of stability time on vertical wicking of polyester fabric at optimized conditions of alkali treatment and various temperatures

5.5 Thermal properties

The differential scanning calorimetry (DSC) thermal analysis technique measures phase changes with heat flow on the substrate under thermal cycle. The results obtained from the DSC of the untreated & at optimized alkali treated polyester fabric stabilized at 20 ˚C and 120 ˚C are shown in figure. 32, 33 and 34 respectively. The treated polyester film show good thermal stability as the curves obtained from DSC are similar to the untreated polyester sample. The stabilized polyester fabrics at various temperatures require only slightly less melting heat that may be due to the surface changes of the polyester fabric after the sodium hydroxide treatment.

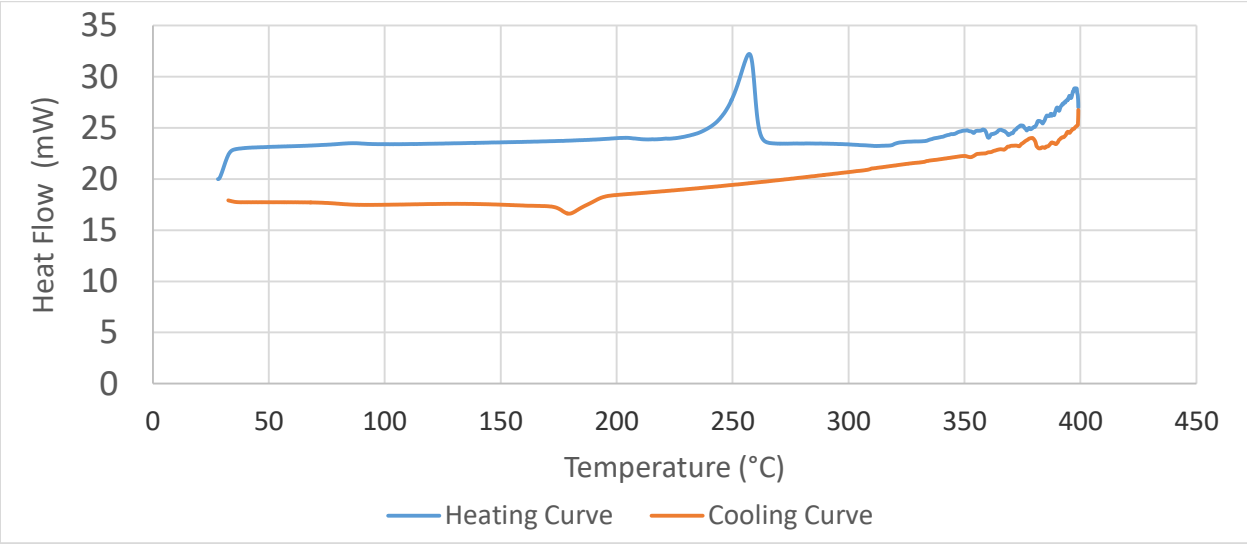


Figure 33. Differential scanning calorimetry of untreated polyester film

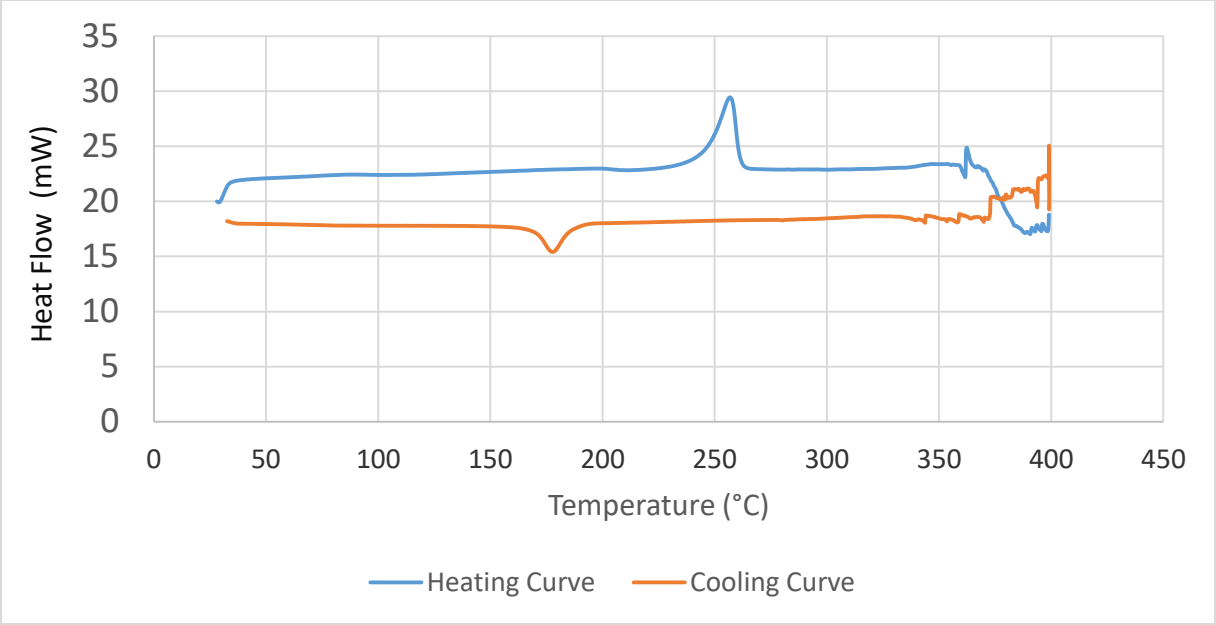


Figure 34. Differential scanning calorimetry of stabilized polyester fabric at 20 ˚C

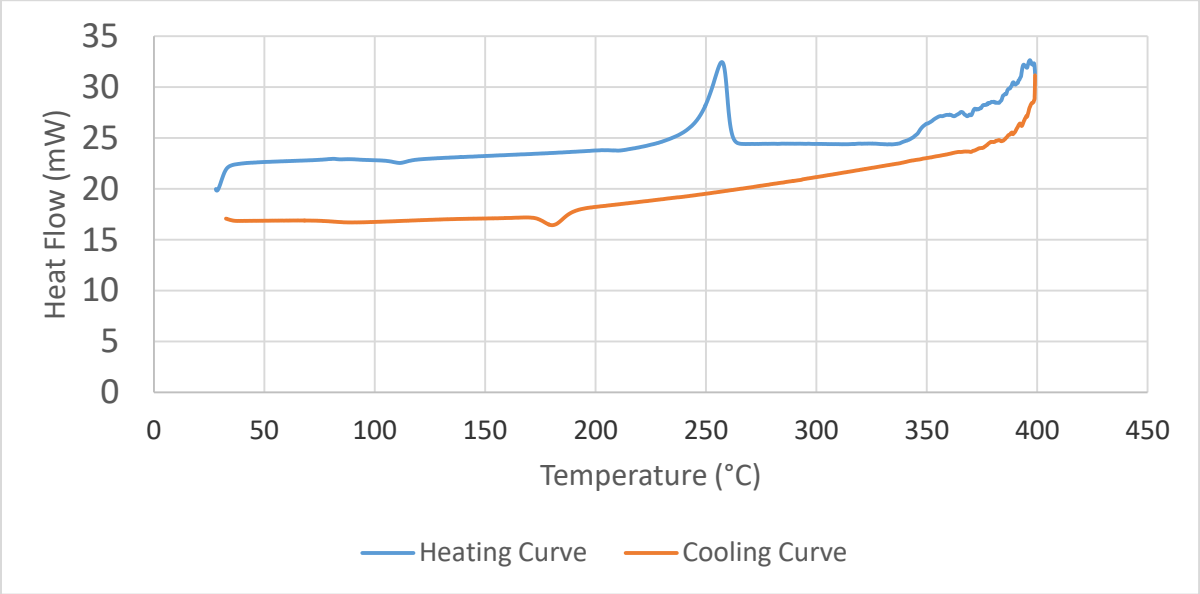


Figure 35. Differential scanning calorimetry of stabilized polyester fabric at 120 ˚C

5.6 Durability of surface hydrophilization against washing cycles

Washing of textiles during service is a compulsory process and it is regulated by chemistry, mechanical agitation, temperature and time. The impact of particular factors can be represented by a washing cycle, within which is the circle dealing with water and fabric that can withstand the washing treatments. The effect of water on individual fibers varies greatly with their chemical

constitution. Hydrogen bonding is perhaps the most important kind of bond between and within fibers that influences stabilization. Cellulose (in cotton), protein (in silk), and polyamide (in nylon) have strong hydrogen bonding networks [91]. Hydrogen bonds that contribute to the transverse structure of the fibers are more or less readily broken and reformed with water molecules. Some fibers such as polyester are substantially unaffected by the absence or negligible presence of hydrogen bonds. The decrease in vertical wicking is only 12 mm from 90 mm to 78 mm, as depicted in figure 35 even after the 15 washing cycles. It indicates that the alkali treatment has the modification of the surface that do not tend to disappear during service.

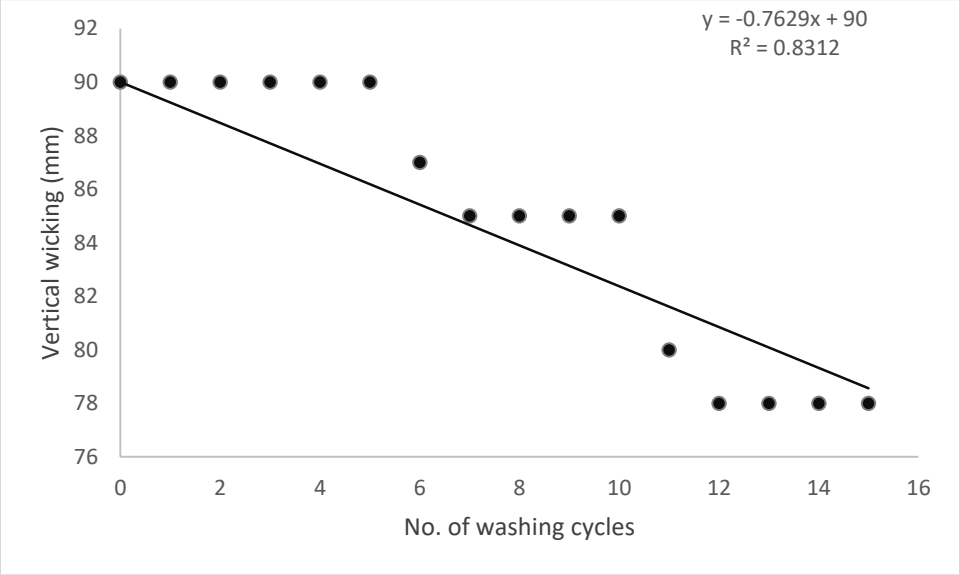


Figure 36. Effect of washing cycles on vertical wicking of surface hydrophilized polyester fabric

5.7 Surface hydrophilization of polyester film

5.7.1 Contact angle

The ideal smooth surfaces that are flat and solid chemically and homogenously there is only one contact angle exists that is at the equilibrium. According to liquid surface tension theory the largest contact angles are measured for water and lower correspond to the diiodomethane. Figure 36 and 37 show the water CA changes for hydrolyzed polyester film as a function of NaOH treatment time for previously treated with 80 % and 75 % sulphuric acid respectively. The surface modification by strong acid causes roughness on the surface of the polymer film that provides a

good surface for the alkaline modification of the polymer film. As the time of treatment of NaOH hydrolysis increases firstly the CA decreases but after some time the CA increases again reaching a value that is less than untreated polyester film. This may be due to the fact that surface treatment by strong acid causes surface activation of polyester film through redox reaction that provides an active surface for hydrolysis by sodium hydroxide but with the increase in the alkaline treatment time the peeling off the surface of polyester causes disappearance of strong acid activation so the hydrolysis is only limited to the alkali. The combined effect of acid and alkali disappears and CA again increases with time reaching a values around 84 that are less than the untreated CA values.

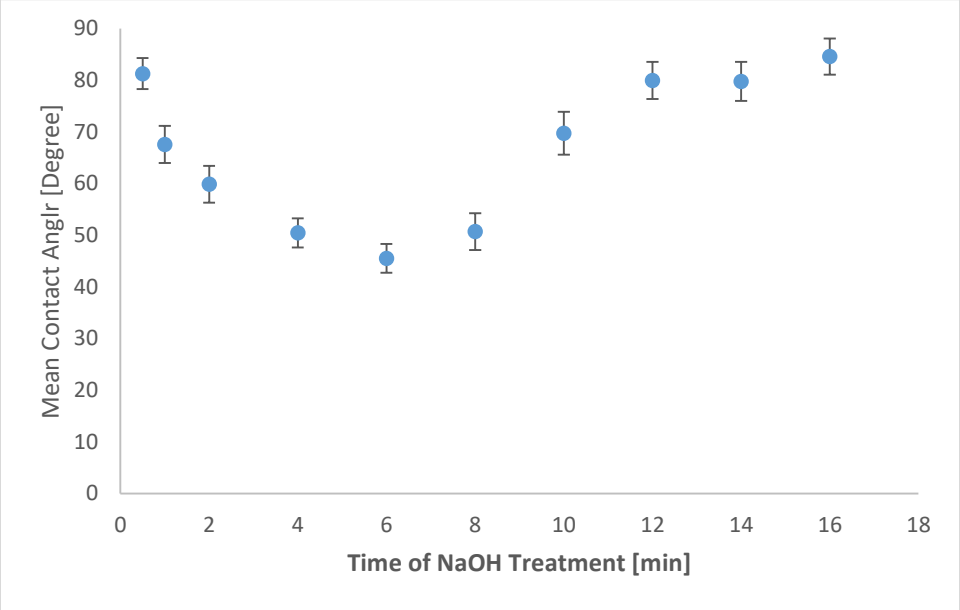


Figure 37. Effect of 50 g/l NaOH treatment time on contact angle of 80 % Sulphuric acid treated polyester film

This small decrease in CA is only caused by alkali treatment only. The combined acid and alkali treatment hydrolyze the surface of polyester as much that the 80 % sulphuric acid treated samples followed by alkali treatment lower the CA value to 45.50 degree after 6 min of treatment while 75 % sulphuric acid treatment lower CA to 57.23 degree. The surface modification increases the surface hydrophilicity of the all the treated samples.

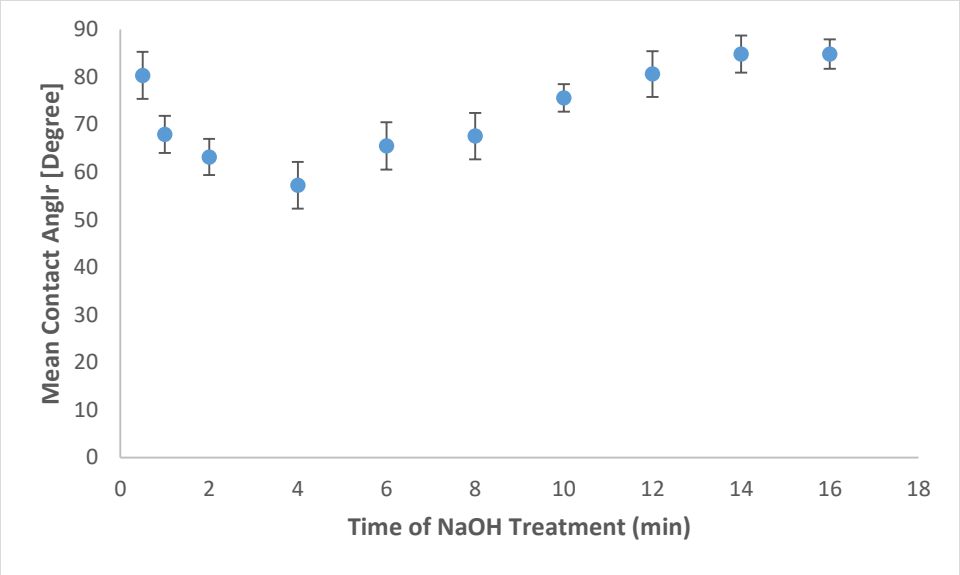


Figure 38. Effect of 50 g/l NaOH treatment time on contact angle of 75 % sulphuric acid treated polyester film

5.7.2 Surface free energy

In this study the CA measurements of three different liquids are further used to calculate the surface free energy of the treated polyester substrate. The surface tension components are given in Table 15.

Table 15. SFE components of polyester substrates untreated and modified with sulphuric acid and sodium hydroxide

mJ m^{-2}	**Owens-Wendt**			**Zisman**	**Li-Neumann**	**Mean**
	γ_S^p	γ_S^d	γ_s	γ_s	γ_s	γ_s
Untreated	0.73	44.10	44.83	36.57	41.79	41.06
S11	4.84	46.78	51.63	43.29	45.04	46.65
S15	16.28	49.01	65.29	47.76	50.75	54.60

When a drop of liquid rests on a solid surface, it makes an angle θ with the surface, the young explained it by the equation below:

$$\gamma_L \cos\theta = \gamma_s + \gamma_{SL} \quad (30)$$

Where γ_s is the surface energy of the solid/air, γ_{SL} is the interfacial tension between solid and liquid and γ_L is the surface tension of liquid/air. Many different methods have been proposed in

order to calculate the γ_s using values of contact angles formed by different liquids with known surface tension. The experimental values of CA at room temperature of water, ethylene glycol and diiodomethane are used to evaluate the SFE of substrates via Owens-Wendt, Zisman and Li-Neumann methods.

Zisman method shows that the cosines CA (θ) formed by drop of homologuos liquids on the solid surface varies linearly with their surface tension. The critical surface tension can then be found by extrapolating the linear function to cosθ = 1, indicating complete wetting ($\theta = 1$). Brethelot uses young equation in order to approximate the SFE by taking into account of work of adhesion for solid-liquid interface by geometric mean and obtained from young equation [92]:

$$cos\,\theta = -1 + 2\sqrt{\frac{\gamma_s}{\gamma_L}} \tag{31}$$

This equation calculates the SFE by using data of CA from one liquid. The use of one liquid may not be reliable and this equation overestimates the pair values obtained from different liquids, usually largely deviating values are obtained by changing the liquids. The Neumann also worked on the transformation of the equation of state for interfacial tension. The SFE is also calculated by method proposed by Li-Neumann [93].

Fowkes approach focuses on the interactions between phases across interfaces and it is based on the theory that the type of forces working between the molecules act independently to each other. The total free energy is divided in two parts, dispersive part and polar part. Owen and Wendt method use this equation and combine the dispersion and polar force components [68]:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2\sqrt{\gamma_S^d\,\gamma_L^d} - 2\sqrt{\gamma_S^p\,\gamma_L^p} \tag{32}$$

Dispersion force and polar components are indicated respectively by superscripts *d* and *p*. from the Young equation it follows that:

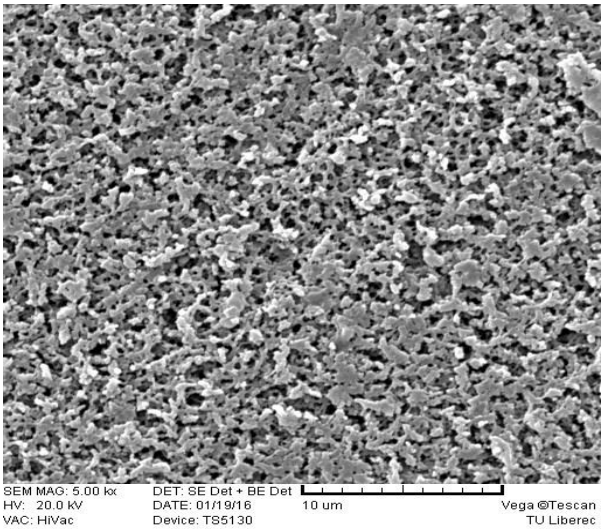
$$\gamma_L\,(1 + cos\,\theta) = 2\sqrt{\gamma_S^d\,\gamma_L^d} + 2\sqrt{\gamma_S^p\,\gamma_L^p} \tag{33}$$

In order to obtain γ_S^d and γ_S^p of a solid surface, the CA measurement of atleast two liquids are required (polar and non-polar).

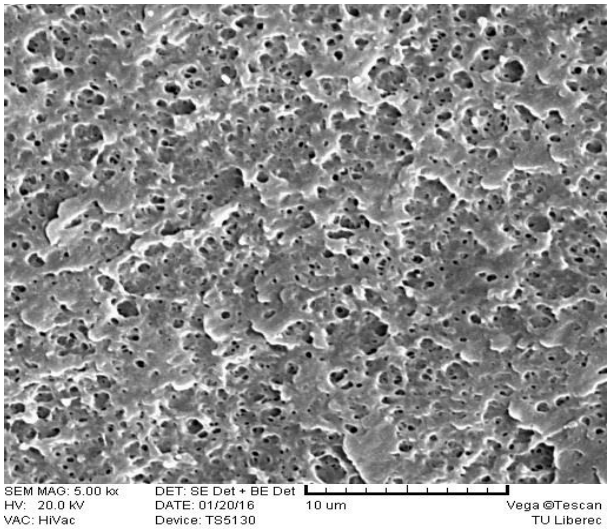
Table 15 shows the SFE energy values of the untreated samples and those which are treated by both sulphuric acid and sodium hydroxide. The critical surface energy values derived by Zisman are lower than that determined by other methods. It is assumed that use of two liquids one polar and other non-polar give better results in calculation of SFE. So the polarity difference between water and diiodomethane is high that gives the better results for SFE calculation. There is definite increase in the SFE of the treated samples. The SFE of the polyester sample treated for 6 min of sodium hydroxide and previously treated with 80 % sulphuric acid has measured to be increase from 41.06 mJ m^{-2} to 54.60 mJ m^{-2} on average of the all the methods used.

5.7.3 Scanning electron microscope (SEM) evaluation

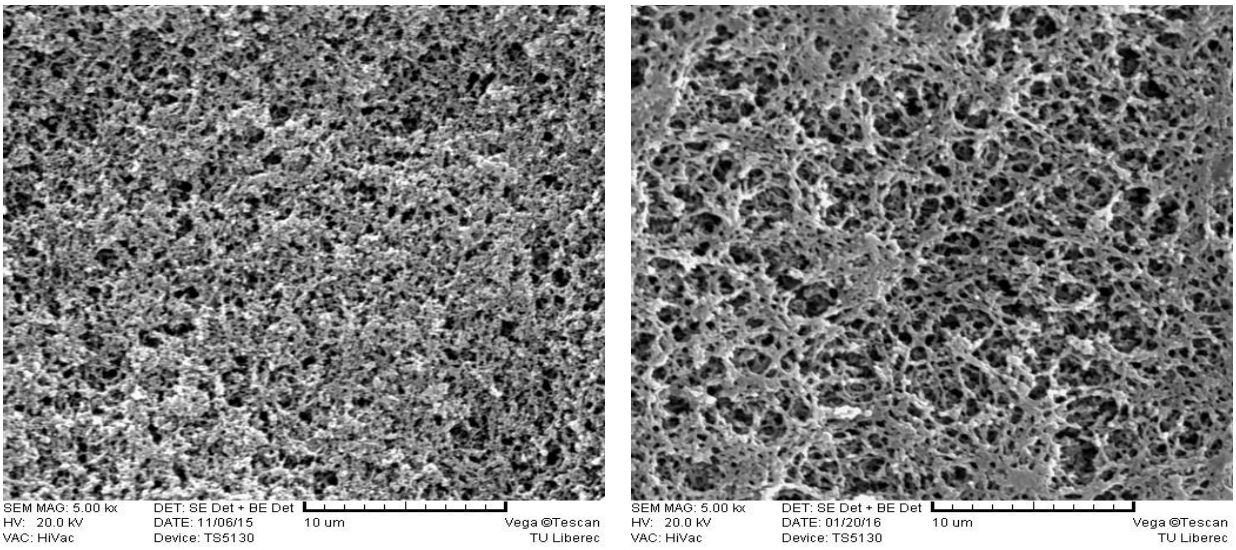
The figure 38 shows the surface topography of the polyester film after the acid treatment and then followed by alkali treatment for the surface hydrolysis of the polyester film. It is clearly evident that the sulphuric acid treatment creates the surface roughness through the acid easter reaction. This surface roughness allows the sodium hydroxide to penetrate in less time and hydrolyse the polyester for the improvement of water retention ability. The combine acid and alkali treatment causes the hydrolysis on the surface of the polyester film making it suitable for the hydrophilicity improvement.



(a)



(b)



(c) (d)

Figure 39. (a) SEM micrograph of polyester film after 80 % sulphuric acid treatment for 3 sec (b) SEM micrograph of polyester film after 80 % sulphuric acid treatment for 3 sec followed by 50 g/l NaOH treatment for 4 min(c) SEM micrograph of polyester film after

5.7.4 T-PEEL test of adhesion

The effect of surface treatment of the polyester film with acid and alkali is tested through T-Peel test of adhesion by using polyurethane adhesive. The N=C=O group present in the adhesive is highly reactive with the –OH group of the treated polyester film. So the increase in the adhesion strength of the treated polyester film can be related to the increase in the surface –OH groups.

The values of the adhesion test is recorded in the force per unit width (kN/m) of the bonded specimen. The values are fluctuated because of the very small area at which the stress is localized during loading. A load curve of the treated and untreated polyester film samples is shown in Fig. 39 T-Peel strength is taken as an average of the center portion of the curve. The T-Peel strength of the treated polyester film is 1.8 times higher than that of the untreated film. This improvement in the adhesion strength shows that the surface modification of the polyester film by hydrolysis is effective in improving the adhesion between polyurethane and polyester film.

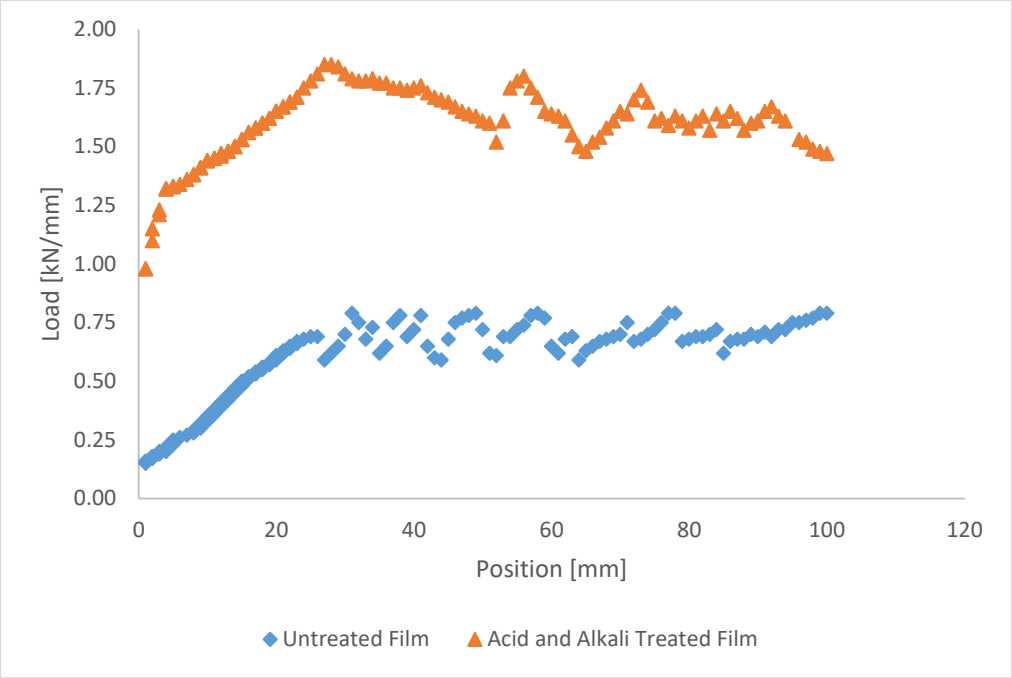


Figure 40. T-Peel test curve of untreated and polyester film treated with 80 % sulphuric acid followed by 50 g/l NaOH for 6 min

5.7.5 Determination of Specific Surface Area

The acid hydrolysis causes some roughness on the surface of the polyester film through hydrolysis. The attack of sodium hydroxide is facilitated, so the knowledge of pore characteristics and specific surface area is required that is determined thorough BET analysis of the treated polyester film. Figure 40 shows the nitrogen adsorption/desorption isotherm of the 80 % sulphuric acid treated polyester film followed by 50 g/l sodium hydroxide treatment for 4 min. A rapid rise in the adsorption-desorption isotherm is observed at low relative pressures and then the isotherm is horizontal at high relative pressures.

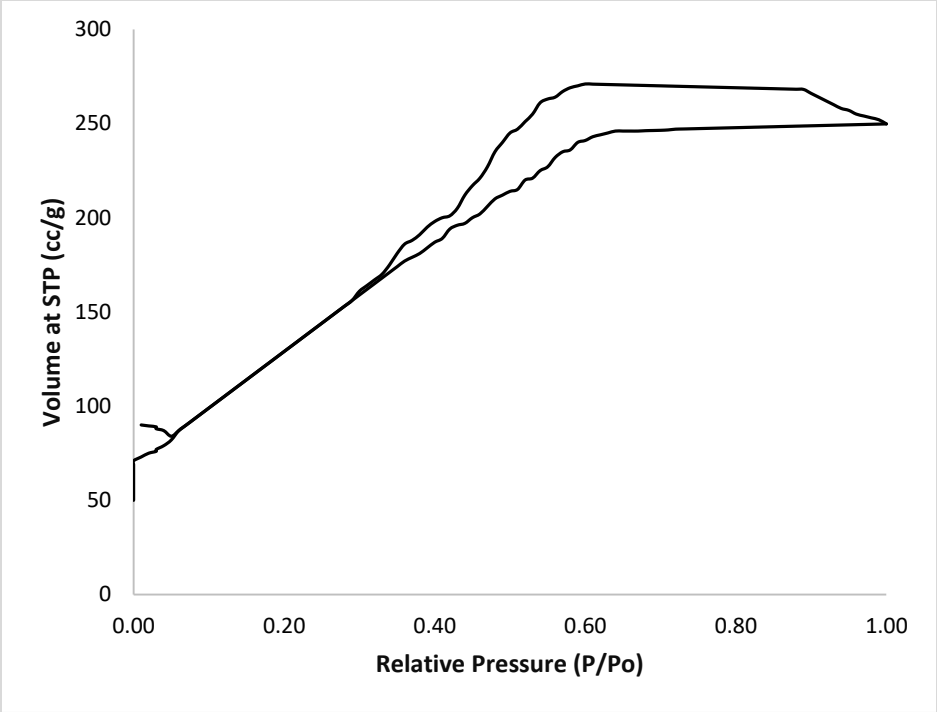


Figure 41. Nitrogen adsorption-desorption isotherm of polyester film treated with 80 % sulphuric acid for 3 sec followed by 50 g/l NaOH treatment for 6 min.

The behavior of the isotherm can be related to the type 1 isotherm based on the classification of the international Union of the Pure and Applied Chemistry (IUPAC) [94]. The type one isotherm confirmed that the micropores are developed on the surface of the treated polyester film. The pore volume and pore diameter of the treated polyester film is found to be 0.417 cc/g and 3.163 nm respectively from BJH analysis. The IUPAC classified pores in three groups: micropore (dimeter < 2 nm), mesopore (2-50 nm) and macropore (> 50 nm) [95]. The treated polyester film dominantly has exhibited mesoporous nature.

CHAPTER 6
CONCLUSIONS AND FUTURE WORK

The following conclusions have been drawn from each study:

6.1 Surface hydrophilization by Pad-dry method

The surface of polyester fabric is successfully hydrophilized by Pad-dry method at low concentration of sodium hydroxide. The influence of sodium hydroxide treatment by Pad- dry method with different low concentrations of caustic soda is studied with different treatment times and compared with the standard caustic treatment at 90 °C with respect to surface morphology, weight loss and wicking height. Hydrolysis with 50 g/l sodium hydroxide using Pad-dry technique causes less surface pitting and thinning of the polyester yarns in the fabric as compared to the standard caustic treatment for 30 minutes. The weight loss by Pad-dry treatment with sodium hydroxide is only 6.78 % with treatment time of 8 minutes while the weight loss by treating polyester fabric at 90 °C for 30 minutes is 27.1%. The time of treatment shows little effect on the wicking height of the polyester fabric treated by pad-dry method. The addition of urea and glycrin in the solution of NaOH for the treatment of polyester fabric has not improved the absorbency properties and also not hinders the alkaline hydrolysis of polyester fabric.

6.2 Optimization of hydrophilized parameters

The higher concentration of sodium hydroxide was found to have positive effect on the percentage weight loss and vertical wicking of the polyester fabric. The time of treatment and temperature of drying relate linearly to the percentage weight loss and vertical wicking of the polyester fabric. The pad dry method at optimized conditions is suitable for the development of surface hydrophilic groups on polyester that leads to the better hydrophilic properties and moisture transmission.

6.3 Durability against different temperature conditions of hydrophilized polyester fabric

The study of thermal stability of the hydrophilized polyester fabric under different performance temperature conditions and for longer periods of time has shown that the sodium hydroxide modified polyester fabric shows better retention of chemical modification at elevated temperatures. The physical treatments like plasma and ozone, that are successfully used to modify

the surface of polyester, tends to reverse the hydrophilic groups as the temperature and time increases during the performance of stages of polyester fabric. The decrease in vertical wicking is 10 mm only even the temperature is increased to 120 ˚C and holding time is six days. The relationship is developed between the maximum suction height (vertical wicking) and holding time. The measured and predicted values shows good agreement when plotted against time.

6.4 Washing fastness properties of hydrophilized polyester fabric

The ability of performance fabrics to withstand the washing cycles is necessary to maintain the effect of surface hydrophilic property achieved by the sodium hydroxide modification of the polyester fabric. The hydrophilized polyester shows good fastness up to washing cycles. The washing of fabric only lowers the vertical wicking to lesser extent.

6.5 Development of hydrophilic polyester film surface by synergistic effect of sulphuric acid and sodium hydroxide

The polyester film is treated with strong sulphuric acid solution and followed by low concentration alkali solution in order to increase surface wettability and adhesion properties. The super hydrophilic surface is obtained by the combined action of acid and alkali at concentration of 80 % sulphuric acid and 50 g/l sodium hydroxide treatment for 6 min. These treatment conditions give the polyester film surface with lowest water contact angle and high SFE values with good adhesion properties. The presence of hydroxyl groups on the surface with significant decrease in the surface energy has been confirmed through contact angle measurements. The SEM and BET analysis has confirmed the increase in roughness after chemical treatment of the polyester film. T-peel data obtained by the polyurethane resin has indicated the increase in adhesion strength after chemical treatment and improvement of adhesion by thermoset resin can be attributed to the increase in surface wettability and roughness due to the surface modification. Finally a super hydrophilic surface of the polyester film can be achieved through combined acid and alkali hydrolysis under controlled conditions.

6.6 Proposed applications and limitations

The proposed application is industrial usage of pad-dry treatment under controlled tension conditions that provides economical usage of water due to low liquor ratios and efficient recycling

of the sodium hydroxide liquors from the padding equipment. It has also good application as longer runs can be processed in at higher speeds with less weight loss and more hydrophilization of the polyester surface. The porous morphology of the polyester film provides super hydrophilic surface that has potential application in the field of flexible electronics and antifogging surfaces where higher adhesion properties are required. The idea of polyester surface modification by synergistic effect of acid and alkali provides a good prospect for adhesion improvement as it requires no sophisticated equipment as most of the physical treatments need for modification.

6.7 Future work

- The moisture transmission rate studies by different methods to study the effect of hydrophilization by this new method.
- The one sided hydrophilization can be done by spray method and it evaluation of extent of hydrophilization.
- Effect of different wicking techniques on the moisture transmission through the polyester fabric.
- The deposition of Nano- cellulosic layers on polyester and their effect on surface wetting of the polymer.

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RESEARCH PROJECTS

- Member of the student grant completion (SGS) project 2014, titled, "Preparation of microporous CMC structure with help of lyophilization", Faculty of Textile, Technical University of Liberec, Czech Republic.
- Member of the student grant completion (SGS) project 2015, titled, "Materials for photodynamic therapy", Faculty of Textile, Technical University of Liberec, Czech Republic.
- Research Assistant in HEC funded project 2011, titled, "Enhancing the cooling and comfort properties of textile clothing through chemical finishing", Faculty of Textile Engineering, National Textile University Faisalabad, Pakistan.